TRANSPORT STUDIES ACROSS THE BIOLOGICAL AND MODEL MEMBRANES

THESIS SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

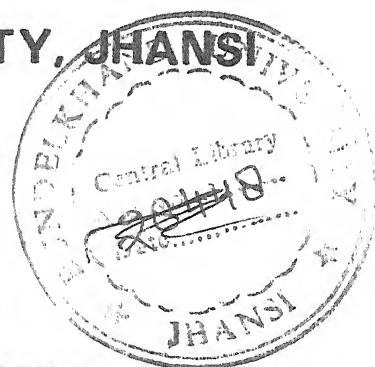# CHEMISTRY

TO THE BUNDELKHAND UNIVERSITY, JHANSI

BY

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POST GRADUATE DEPARTMENT OF CHEMISTRY

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DEDICATED TO THE SWEET MEMORIES
OF MY BELOVED MAMU
LATE Jb. AHMAD IRPHAN ANSARI

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CERTIFICATE

This is to certify that Mr. MOHD. AYUB ANSARI has carried out the research work under my supervision and guidance in the post graduate department of Chemistry, Bipin Bihari College, Jhansi for the thesis entitled "TRANSPORT STUDIES ACROSS THE BIOLOGICAL AND MODEL MEMBRANES". He has put in more than 200 days in the department as required by the Bundelkhand University ordinance during the research period. The thesis being submitted to the Bundelkhand University consists of the original research work and is suitable for the award of Ph.D. degree in chemistry.

5th OCT.1992

(DR. R.S. Kushwah)

DECLARATION

I hereby declare that the thesis intitled "TRANSPORT STUDIES ACROSS THE BIOLOGICAL AND MODEL MEMBRANES" being submitted for the degree of "DOCTOR OF PHILOSOPHY" to the Bundelkhand University, Jhansi (U.P.), is an innovative piece of work carried out with utmost dedication by me, and to the best of my knowledge and belief it has not been submitted elsewhere.

Jhansi :. October 5, 1992

(Mohd. Ayub Ansari)

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(MOHD AYUB ANSARI)

CONTENTS

GENERAL
INTRODUCTION

A precise and complete definition of the word "membrane" is difficult to make (1) and any complete definition given to cover all the facets of membrane behaviour will be incomplete. According to Sollner (1,2) "A membrane is a phase or structure interposed between two phases or compartments which obstructs or completely prevents gross mass movement between the latter, but permits passage, with various degrees of restriction, of one or several species of particles from the one to the other or between the two adjacent phases or compartments, and which there-by acting as a physicochemical machine transform with various degrees of efficiency according to its nature and composition of the two adjacent phases or compartments". In simple terms it is described as a phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquids and /or vapours contacting the two surfaces (3). The term hetero-geneous has been used to indicate the internal physical structure and external physicochemical performance (1,4-6) from this point of view most membrane in general are to be considered heterogene-ous despite the fact that conventionally, membranes prepared from coherent gels have been called homogeneous (7).

The notation of homogeneous Vs. heterogeneous mem-branes proves to be an important distinction from the point of view of mass transport. In the dilute solution limit the friction coefficients for mass transport by diffusion or migration are interconvertible by Onsager reciprocal relations, and both can be related to jump distance and frequencies according to random walk

models. As long as there are no preferred regions of low friction in the membrane, it is isotropic on a molecular level and is considered to be homogeneous. Uniformity of mesh on a molecular scale is another view of homogeneity. Channel free solid and liquid membranes are usually homogeneous, and two phase membranes such as crystallites imbedded in non ionic resin are clearly heterogeneous. The distinction, however, is not always essential (7).

Membrane may be solid, liquid or gas(8) and the outer phases are usually liquid or solid . Membranes are usually thin in one dimension relative to the other two dimensions. This property is only functional or operational. In order to achieve a measurable chemical change or electrochemical effects and to make chemical or electrochemical measurements on a membrane system in a reasonable time, some transport related property must be susceptible to temporal change. Thus, a change in potential, flux, or concentration (among many varying and measurable quantities) requires membrane thickness d such that $d^2/2D$ is comparable with the observation time (D is a mean diffusion coefficient). Although irregularly shaped membranes are conceivable, most theories and experiments are restricted to systems with one dimensional or spherical symmmetry such that transport occurs in one dimension , the x direction in parallel-face planar membranes or along a radius in membranes with spherical shape.

Membranes are considered to be porous or nonporous

depnending upon the extent of solvents penetration (9). At the non porous extreme or membranes which are non ionic and cation negligible transportable species at equilibrium. Ceramics, quartz,anthracene crystals, and teflon films between metel electrodes or electrolyte bathing solutions are solid membrane examples .Organic liquid films such as hydrocarbons and fluorocarbons in contact with aqueous electrolytes are liquid membrane examples. At the other extreme are porous membranes , which can be solvated and will contain components from the other phases. Among these are nonionic film such as cellophane , inorganic gels, and loosely compressed powders in contact with aqueous solutions. These material absorb solvent from the surrounding media and may also extract other neutral molecules and ionic salts . Biological membranes such as pig bladders, was given by John L. Anderson (10)in the review to trace some of the early history of membrane transport. Moreover , H.Arif et al. (11) also took the transport of metal ions across pericardial membrane.

More recently H.K.Lonsdale in his editorial (12)has put the definitions of the membrane given by various eminent scientists in the field of membrane. According to Lonsdale,the McGraw-Hill Dictionary of Scientific and Technical Terms (2nd Ed.) it is said,"Membrane (Chem. Engg.) 1. the medium through which the fluid stream is passed for purposes of filtration. 2. the ionexchange medium used in dialysis ,diffusion , osmosis and revers osmosis and electrodialysis". Moreover ,John A.Quinn, of

the university of Pennsylvania, Philadelphia, Pennsylvania, and the member of the same editorial board defined the membrane as : A membrane is an interphase. It has distinct physicochemical properties and it is bounded by two surfaces, each of which joins it to a contiguous bulk phase . Generally it is "thin " in the sence that it has a large ratio of surface area to volume ; as it's thickness approaches moleculer dimensions the interphase becomes an interface. The special separative/barrier/contacting properties of membranes derive from the fact that an interphase can communicate simultaneously with its two adjacent phases; this permits the establishment maintenance of gradient across the membrane and allows exchange to occur at both surfaces.

More widely studied are the membranes of polyelectrolytes, aqueous (3,13-15) immiscible organic liquid electrolytes. Various parchment supported inorganic precipitates (16-29), solid ion conducting electrolytes including silver halides, rare earth fluorides, and alkali silicates and alumino-silicate glasses (30-33) all these materials contain ionic or ionizable groups within the membranes which are capable of transport under diffusive or electric field forces. In addition, these materials possess the property of porosity. Polyelectrolytes tend to swell rapidly by osmotic pressure driven uptake of solvent. Liquid ion-exchangers are surprisingly slow to take up water, while the inorganic salts have no tendency to hydrate. Glass membranes are complicated by simultaneous hydrolysis of the polyelectrolyte

during uptake of water (34-36). Nafion 120 membrane (37) for the efficiency of energy conversion in separatron processes following theories are based on irreversible thermodynamics. Similarly S.T.Hwang et al. (38) characterized silicon based inorganic membrane for gas separation.

Depending on the dielectric constant and solvent penetration, sites are potentially, partially, or even completely ionized. A characteristic of electrolyte membranes is the presence of charged sites (13,39-41). The charged sites of the membranes are due to the attach of cations or anions. Membranes without ionizable groups contain no charge sites. It is important to know that cellulose triacetate, which is initially site free, soon develops negative sites by hydrolysis and oxidation on exposure to aqueous solutions.

The frequent use of "charged" and "uncharged" in the membrane literature is usually unsound electrostatically, but does provide an intuitive chemical description. For example, "charged" membrane usually refer to electrolyte membranes such as solid and liquid ion exchangers where the fixed and mobile sites are the "charges". Actually, these membranes are quasi-electroneutral in their bulk when the thickness is large compared with the Debye thickness at each interface. Quasi-electroneutrality means that in any volume element large as compared with the distance between ions, the sum of ionic charges $\Sigma_i Z_i \overline{C}_i = 0$. In the literature,"uncharged" membranes are those, like cellophane, with

no fixed charges. This frequently used litrature definition provides no place for lipid bilayer membranes, which are electrostatically neutral only in the absence of charge carriers and in the absence of bathing solutions whose salts possess preferential solubility of anion over cation or vice versa, but are usually electrostatically charged by an excess of ions of one sign in normal operation. Thick hydrocarbon membranes and membranes of diphenyl ether (or derivatives),phthalate, and sebacate esters are generally neutral in the presence of most bathing electrolytes, but may be charged electrostatically depending on thickness, in the presence of neutral carrier species which preferentially solubilize ions of one sign. The use of "charged" and "uncharged" to describe electrolyte or non electrolyte membrane has been discouraged unless the precise electrostatic connotation is involved (7).

Membranes may be broadly classified into two classes that is natural and artificial. Natural membranes are classified to possess a fundamental unit membrane structure which is a bimolecular leaflet of lipid with their polar groups oriented towards the two aqueous phases of the cell and protein is supposed to exist close to the polar heads of the leaflet. This type of the universal structure is absent in artificial membranes. Eisenman et al. (42) have given a classification of these membranes based on their structures.

Unlike the classification based on membrane structure,

membranes are usually classified either on the basis of their
nature, i.e., coherent gel or otherwise or on the nature of the
chemical reaction invloved in their formation, i.e., addition or
condensation reaction. The efforts of various workers have been
directed towards : (A) preparing membranes with good chemical and
mechanical stability and favourable electrical performance suit-
able for fundamental transport studies and for applications in
some industrial operations such as the treatment of brakish
water, saline water conversion, etc., (B) building suitable
models to mimic the properties of natural membranes, and (C)
preparing composit membranes containing cationic and anionic
groups in suitable arrangement to demonstrate and to study the
physicochemical phenomena associated with the rectification of
alternating current and other special membranes for specific
purposes. It is worthwhile to mention that most of the work
concerning catagory (A) seems to be directed towards finding
suitable membrane materials for fabricating a structure for
effective desalting sea water by application of pressure. The
most commonly used materials for casting a membrane for desalina-
tion is cellulose acetate although, Polymethacrylic acid (PMA),
Phenol sulphonic acid (PSA), Polystyrene sulphonic acid (PSSA)
and cellulose esters have proved very useful (43). A number of
investigators in recent years have prepared membranes from cellu-
lose accetate under varying conditrons and used them to under-
stand the mechanism of water flow (44-61). In catagory (B) bilay-

er membranes, first generated by Mueller et al.(62) have most widely been used as model for living cells and the studies have given somewhat a better understanding of the structure and function of the natural membranes. The membranes of catagory (C) are quite numerous (7,63-66).

Transport processes occuring across artificial membranes separating different solutions have attracted the attention of chemists, chemical engineers and biologists etc. Chemists and chemical engineers would like to understand the mechanisms of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists, however, would like to use them as simple models for the physiological membranes in order to understand the behavior of complex cell membranes in terms of established physicochemical principles. The recent progress pertaining to membrane diffusion and transport problems have been achieved in varying fields like Chemistry, Biochemistry, Physiology, Pharmacology, Biophysics and Industrial chemistry etc in which the starting points and aims have been different. Surface chemistry, Solution theory, Colloid chemistry, Electrochemistry and Thermodynamics etc. have been employed to understand the mechanism of transport in living cells, desalination and electrodics. There are several areas of membrane research which have potentially far-reaching consequence to medicine and chemical industry. Work in this field is contributing significantly to the economic prosperity and physical

wellbeing of all mankind.

The literature in book form describing membrane technology and applications is far too extensive to mention. The principal volumes containing significant sections on, or totally devoted to membrane electrochemistry are by Clarke and Nachmansohn(67),Helfferich (13), Spiegler (44-45), Merten (46), Marinsky (68), Stein (69), Cole (70), Lakshminarayanaiah (14,43,63), D.R.Smith, R.J.Lander and J.A.Quinn (71), Arnat and Roper (72), Kotyk and Janacek (73), and others. Continueing series are edited by Bittar (74), Eisenman (75), Danielli, Rosenberg and Cadenhead (76),H.K.Lonsdale and H.E.Podall (77). Applications of membrane electrochemistry to yield activity sensing electrodes are amply described in books edited by Eisenman (30) and in recent reviews (78,79). However, this field has produced such a variety of new measuring devices and has opened so many analytical possibilities in terms of new analysis and new detection systems that it is very likely that additional volumes will soon appear. Numerous recent volumes are concerned, in part, with membrane electrochemistry (80-88).

Current membrane theories have been classed by Schlögl (89) into three groups: (i) Theories based on the Nernst-Planck fulx equations or their refinements, (ii) theories using the principles of nonequilibrium thermodynamics, and (iii) theories using the rate processes.

This grouping attempts to classify the various math-

matical approaches, according to the ideal models on which they are based. It is in fact too schematic, as many theories occupy intermediate positions. No author is likely to take the view that one of these treatments is right and the others wrong. The various descriptions supplement each other and depending on the system under consideration, one of the three will prove the most suitable. It may be shown, for example, that when the number of activation thresholds becomes very large, and the distance between the lattice points sufficiently small, then groups (iii) and (ii) merge into each other. A transition is also found between groups (i) and (ii) (89).

Unlike group (iii), groups (i) and (ii) can be classified in the general scheme of irreversible thermodynamics. In group (i) as well as in group (ii), linear relationship are assumed between the particle fluxes and the driving forces owing to the differing characters of the driving forces, group (i) is treated according to the method of "discontinuous systems", and group (ii) according to that of "continous systems". An integration in group (ii) across the membrane does not as a rule yield a linear relationship between the flux and the general chemical potential differences. Only for sufficiently small differences does group (ii) merge into group (i) after integration. In this sense group (ii) is more general than group (i). Group (ii) is, however, inferior to group (i) in that a number of idealizations must be assumed before an explicit integration can be affected.

Kirkwood (90) finds a correction between group (i) and (ii). His initial flux equation differs from that normally used in the treatment of "continuous systems" in irreversible thermodynamics. This treatment of Kirkwood has been developed and modified by schlögl.

The theories of the first group have the advantage of being relatively simple. For ion-exchange membranes, however, they are often inadequate. These theories deal chiefly with processes occuring within the membrane. For such a purpose the theories of the second group are proper choice.

The most important theories of the second group are based either on quasi-thermodynamics or on thermodynamics of irreversible processes. The fundamental difference between these two approaches are summarized below.

Quasi-thermodynamics is not interested in particle fluxes. One might say that the quasi - thermodynamic approach consists in taking a snapshot of the system and calculating emf from the charges which a reversible electric current would produce in the system if it were "frozen" in the state in which the photographic picture was taken. The procedure gives directly the emf of the cell. No model is needed. Taking the snapshot, however, is often not as simple as it may seen. A rigorous treatement would require the knowledge of the composition of every differential layer of the diffusion zone (i.e. the concentration profiles of all species). Scince obtaining this information experimental-

ly is usually too lengthy a task or even quite impossible, the quasi-thermodynamics treatement is forced to make assumption about the condition of the system.

The thermodynamics of irreversible processes (91) in contrast to quasi - thermodynamics does not require prior knowledge of the concentration profiles. The set of equations of thermodynamics of irrversible processes interrelates all accuring "fluxes" (of species electric current, heat etc.) and "driving forces" (gradients of chemical potential, electric potential, temperature etc.). From measurements of a sufficient number of "phenomenological coefficients", all fluxes and forces and hence also the emf can be calculated, without knowledge of the profiles and without using the concept of "reversible energy production" on which quasi - thermodynamics is based. Furthermore, thermodynamics of irreversible processes is applicable also to nonisothermal systems and includes coupling of fluxes which is not covered by quasi - thermodynamics. It may be mentioned here that the discipline of irreversible thermodynamics provides a precise mathematical discription of the processes of the tronsport and diffusion in membrane systems. Its application to membrane processes is a natural development of the basic theory of Onsagar (92) and has been developed by Staverman (93), Kedem (94), Katchalsky (91), Caplan (95), Mears (96), Spiegler (44,45), Rastogi (97), Anna Narevska (98), B.Baranowski (99), F.A.Siddiqi (100) and others in an extensive and expanding literature.

Several investigators have applied the theory of obso-
lute reaction rate to diffusion processes in the membranes.
Zwolinski, Eyring and Reese (101) examined the non electrolyte
permeabilities data for various plant and animal cells by apply-
ing the diffusion processes as one of the basic phenomena. They
presented a detailed kinetic approach to diffusion which clari-
fies much established concepts and provide impetus to a fresh
approach to the problems in the field of biological diffusion. It
is equally adoptable to the treatment of the permeabilities of
membranes to electrolytes, to nonelectrolytes under the driving
forces of a concentration gradient, activity gradient, and exter-
nal and internal potential gradients. Zwolinski, Eyring and Rees
(101) treatise on membrane diffusion is based on the "activated
state" or the "transition state" theory. Beg et al. (102,103)
applied absolute reaction rate theory to investegate the mecha-
nism of transport of simple metal ions through the parchment
supported membranes as well as their selectivity ratio on the
membrane surface. Samanta and Basu (104) used the absolute reac-
tion rate theory for the calculation of some thermodynamic param-
eters in order to consider the energetics of electrolyte permea-
tion in microporous membranes.

Laidler, Dames and Shuler (105) have also considered
the kinetics of membrane permeation for nonelectrolytes through
collodion membranes. They also developed flux equations for sol-
vent and solute especially as a function of the osmotic and

hydrostatic pressure across the membrane. Tien and Ting (106) have recently applied the theory of reaction rates to diffusion processes through Bilayer Lipid Membrane (BLM) and various thermodynamic quantities like free energy of activation, enthalpy of activation and entropy of activation have also been drived. Recently Kimikuza et al. (107) using energy barrier theory determined that diffusion coefficient of the metal ions in the membrane phase are proportional to the activity of ions in the external metal ions solution. Moreover, Samanta (108) used absolute reaction rate theory to determine energetics and the activation parameters for the measurement of anions in the microporous membranes. B.Baranowski(99) applied the non equlibrium thermodyanamics to membrane transport in order to explain the transport phenomena in membranes. It can be investigated by different experimental methods leading to a rich variety of measurable quantities, the compactness and selectivity of a phenomenological description are of great value. Yusuke Imai (109) outlined a module of membrane transport system moduled by network thermodynamics in two steps : one using the bond graph method of network thermodynamics, resistive and capacitive modules expressed sub systems as integrated cercuits. In the second step the membrane transport system was designed from a combination of the resistive module and the paired capacitive modules as sub systems.

In the membrane studies application of electrochemistry is pertinent at three lavels (7). One is the development of

techniques with application to experimental phenomenology including current-voltage-time-concentration behaviour. A second is the mathematical modeling implied by experiment and tested against experiment. The third level is experimental verification of models in terms of the molecular processes and properties which includes determination of theoritical parameters by electrical methods and by complementry nonelectrochemical methods: Physical, optical, ESR, NMR, Raman, fluorescence, T-jump techniques etc. The most important contribution of electrochemists to membrane electrochemistry is the transfer of perspective and wisdom to the new area. There are many sine qua nons in electrochemistry which have occured through extensive studies of electrolytes and electrolyte/membrane interfaces. Electrochemists have learned to subdivide systems into interfacial and bulk processes and to expect effects of dielectric constant (Complex formation, ion pairing), effects of short-range forces (adsorption of charged and uncharged species with, possibly, changes in rates of interfacial processes), effects of high fields near surfaces (wien effect, and dielectric saturation), and the important effect of local potentials on rates of interfacial processes (irreversible charge transfers, psi effects, etc). Application of membrane potential equations to Tight Epithelia and by G.M.Lyndsay et al. (110,111) also reported the contribution of secondary active transport processes to membrane potentials.

In this thesis transport properties across synthetic

and boilogical membranes when they were used to separate various aqueous electrolyte solutions are reported. Membrane electrolyte system has been considered to contain four chemical species, 1-counterion, 2-coion, 3-water and fourth the membrane matrix which carries fixed charg group and excludes the possibility of chemical reaction within the membrane. The membrane, therefore, has been considered to constitute the repeat unit of the matrix due to the fixed charge and adjacent polymer segments. It is, therefore, possible that kinetic coupling interaction of membrane matrix will include not only the contribution of fixed charge but also specific polymer effects if such exist. This is an important qualification to the description of the species four as simply as ion, although it appears from earlier studies that such effects are small (112-114).

The thesis has been presented under the following three heads.

1. MEMBRANE CHARGE DENSITY:
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This portion of the thesis deals with the measurements of membrane potential across the parchment supported mercuric sulphide, nickel sulphide membranes and Hen egg shell biological membrane using various 1:1 electrolyte at different concentrations under isothermal conditions for the evaluation of themodynamically effective fixed charge density of the membrane as well as to examine the validity of the recently developed theories for membrane potential based on the thermodynamics of irreversible

processes. The observed membrane potentials are used to evaluate the effective fixed charge density of the membranes, transport number of cations across the membranes in order to characterize them.

2. MEMBRANE SELECTIVITY:

In this portion of the thesis, the evalution of membrane selectivity of the above membranes towards simple ions using biionic and multiionic potential measurements has been carried out for various 1:1 electrolytes. Membrane conductivity measurements have also been used to substantiate these findings.

3. TRANSPORT MECHANISM OF SIMPLE METAL IONS THROUGH MEMBRANES :

In this chapter the conductance behaviour of parchment supported mercuric and nickel sulphide membranes bathed in different concentrations of alkali metal chloride at different temperatures has been studied. Absolute reaction rate theory has been applied in order to investigate the transport mechanism of simple metal ions through the membranes.

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CHAPTER-I

MEMBRANE CHARGE DENSITY

INTRODUCTION

One of the most consistent properties of biological system is the presence of a voltage across the cellular surfaces. The mechanism whereby this potential arises is still in dispute. Some consider it to be a diffusion potential while other suggest the voltage to be an adsorption potential(1).Teorell (2,3) considered the presence of charge on the membrane skeleton responsible for the development of potential across it. Based on fixed charge concept a number of theoritical equations for membrane potential, developed across a charged membrane separating two electrolyte solutions, have been derived and tested using, generally synthetic (model membranes) and egg shell membranes. However, the various attempts made to calculate membrane potentials fall into three groups: (a) the idealized theory of Teorell-Meyer-Sievers (TMS) (4) and its refinements (5), (b) the pseudothermodynamic approach due to scatchard and treatment based on the thermodynamics of irreversible processes (6) and (c) kinetic approach based on the theory of absolute reaction rate.

A potential difference is generally established between two electolyte solutions at different concentration separate by an ion-permeable membrane.This potential difference, called the membrane potential,plays an important role in electrochemical phenomena observed in various biomembrane systems. As is well known, in the stationary state the membrane potential arises both from the diffusion potential (7,8) and membrane

boundary potential (9-12).

In this chapter, the evaluation of effective fixed charge density of hen egg shell biological membrane and inorganic precipitate mercuric sulphide and nickel sulphide parchment supported membranes from membrane potential measurements which are based on thermodynamics of irreversible processes of Kobatake et al. (13-21) and Nagasawa et al.(22) including the generally used and widely accepted method of TMS (4) are described. This is in order to substantiate our earlier findings, on the basis of Eisenman-Sherry model of membrane selectivity, that egg shell membrane and parchment supported membranes possess small density of fixed charge groups on the membrane matrix, as well as to test the validity of the recently developed theories for membrane potential.

EXPERIMENTAL

Parchment supported mercuric sulphide,nickel sulphide membranes were prepared by the method of interaction suggested by Beg, Shyam and Coworkers (23,24). To precipitate these substances in the interstices of parchment paper, a 0.2M solution of sodium sulphide was placed inside glass tube, to one end of which was tied the parchment paper (supplied by M/S Baird and Tatlok London Ltd.) previously soaked in water. The tube was suspended for 72 hours in a 0.2M solution of either mercuric chloride or nickel (II) chloride. The two solutions were interchanged later and kept for another 72 hours. The membranes thus prepared were washed

with deionized water to remove free electrolytes.

The egg shell membrane was isolated from the freshly laid hen egg. The egg was broken first at one end. Yolk and white of the egg were poured out. The egg membrane was then separated gently from the hard $CaCO_3$ covering. The shell membrane consisting of two layers a thick outer next to $CaCO_3$ shell and a thinner next to the albumin(3), was washed several times with deionized water in order to remove water soluble substances, these membranes were then clamped separately between two half cells of an electrochemical cell of the type

Reference electrode	Solution C_2	Membrane	Solution C_1	Reference electrode
		Diffusion potential		

Donnan potential   Donnan potential

for the measurement of membrane potential $Hg-Hg_2Cl_2-KCl$ was used as a reference electrode. The total potential difference between reference electrode placed on either side of the membrane is the algebraic sum of the electrode potential, i.e., concentration potential and the membrane potential E_m (25,26). A tenfold difference in concentration of chloride solutions (i.e; $C_2/C_1=10$) was maintained and measurements were made by a pye-precision potentiometer (No.7568). The solutions were replaced by fresh solutions and when there was no change in potential with the addition of fresh solution, with constant vigrous stirring by a pairs of

magnetic stirrers, it was taken as the true total potential difference across the $Hg-Hg_2Cl_2-KCl$ electrodes. In all the membranes it could be reproduced within a few tenths of a mV. The whole cell was immersed in a water thermostat maintained at $25\pm0.1^{O}C$. The various salt solutions (chlorides of Li^{+}, Na^{+} and K^{+}) were prepared from BDH, AR grade chemicals and deionized water.

RESULTS AND DISCUSSION

The values of membrane potential E_m measured across parchment supported mercuric and nickel sulphide membranes and hen egg shell membrane in contact with various 1:1 electrolytes are given in Tables 1.1-1.3. These membrane potential values are plotted in Figs. (1.1-1.3) against log $(C_1+C_2)/2$.

When two electrolyte solutions at different concentration are separated by a membrane the mobile species penetrate the membrane and various transport phenomena are induced in the system (18). Membranes in general have the ability to generate potentials when they are used to separate electrolyte solutions of different concentrations. This property is attributed to the presence of a net charge (23,24,26-33) probably due to adsorption of anions or cations. The quantity of charge required to generate potentials, particularly when dilute solutions are used, is small. This, of course, is dependent on the porosity of the membrane. If the membrane pores are too wide well defined potentials can not be obtained. But if the membrane pores are small, a

magnetic stirrers, it was taken as the true total potential difference across the $Hg-Hg_2Cl_2-KCl$ electrodes. In all the membranes it could be reproduced within a few tenths of a mV. The whole cell was immersed in a water thermostat maintained at $25\pm0.1^{\circ}C$. The various salt solutions (chlorides of Li^+, Na^+ and K^+) were prepared from BDH, AR grade chemicals and deionized water.

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TABLE 1.1

EXPERIMENTALLY OBSERVED VALUES OF MEMBRANE POTENTIAL E_m (mV)

ACROSS MERCURIC SULPHIDE MEMBRANE IN CONTACT WITH VARIOUS 1:1
ELECTROLYTES AT $25\pm0.1\ ^{\circ}C$

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (M)			
1.0/0.1	1.42	-3.78	-15.20
0.5/0.05	3.38	-3.08	-14.53
0.1/0.01	11.32	6.02	-13.39
0.05/0.005	16.10	8.94	-5.95
0.01/0.001	29.60	20.95	12.17
0.005/0.0005	36.37	24.00	20.95
0.001/0.0001	37.75	24.22	21.75

Vide Fig. 1.1
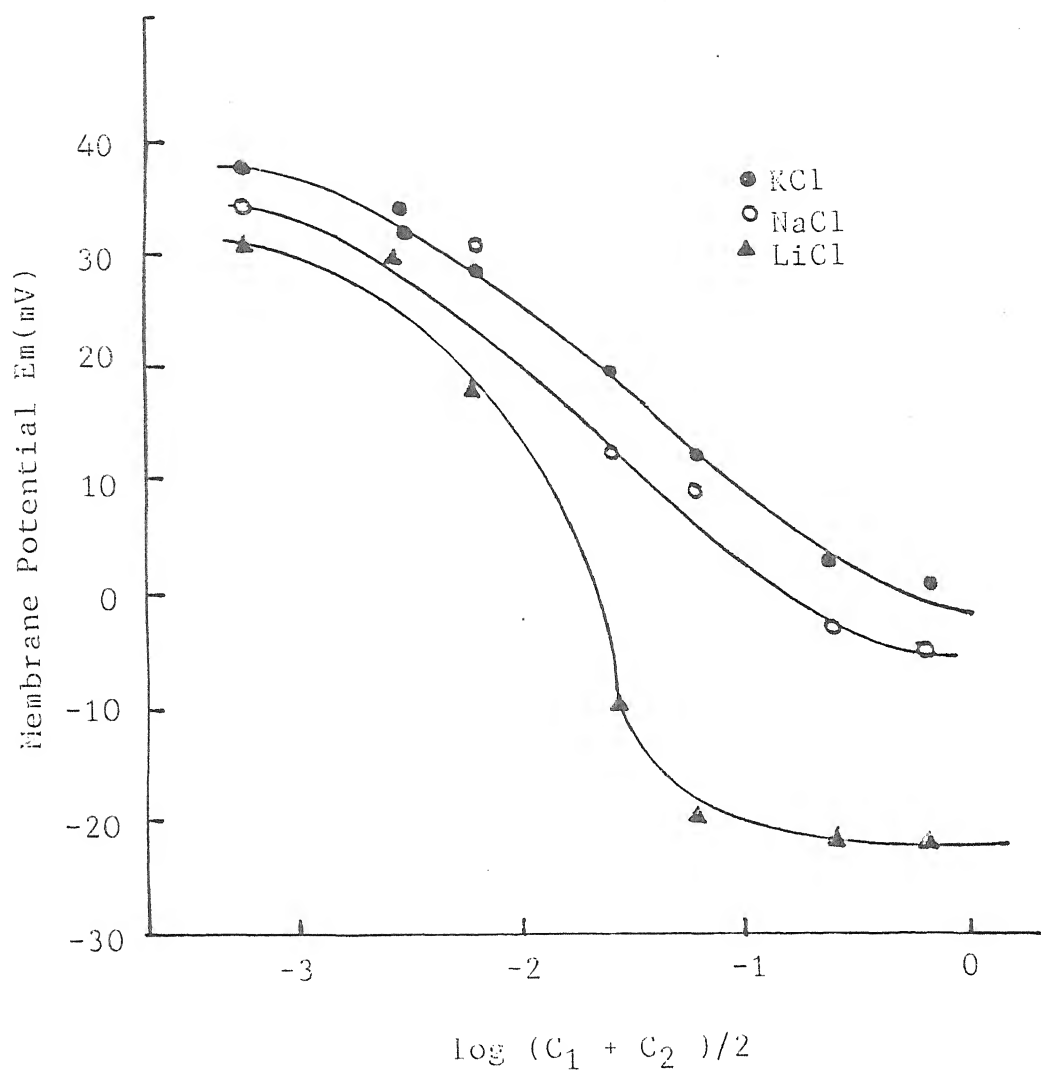
Fig.1.1. Plots of membrane potentials Em(mV) against
log $(C_1 + C_2)/2$ using 1:1 electrolytes across
mercuric sulphide membrane

TABLE 1.2

EXPERIMENTALLY OBSERVED VALUES OF MEMBRANE POTENTIAL E_m (mV)
ACROSS NICKLE SULPHIDE MEMBRANE IN CONTACT WITH VARIOUS 1:1
ELECTROLYTES AT $25 \pm 0.1\ ^{\circ}C$

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M) C_2/C_1			
1.0/0.1	2.3	-5.3	-11.1
0.5/0.05	3.3	-3.9	-10.8
0.1/0.01	20.8	5.5	0.0
0.05/0.005	22.4	10.7	5.4
0.01/0.001	31.0	24.9	20.3
0.005/0.0005	37.0	26.4	25.2
0.001/0.0001	37.2	26.5	26.0

Vide Fig. 1.2
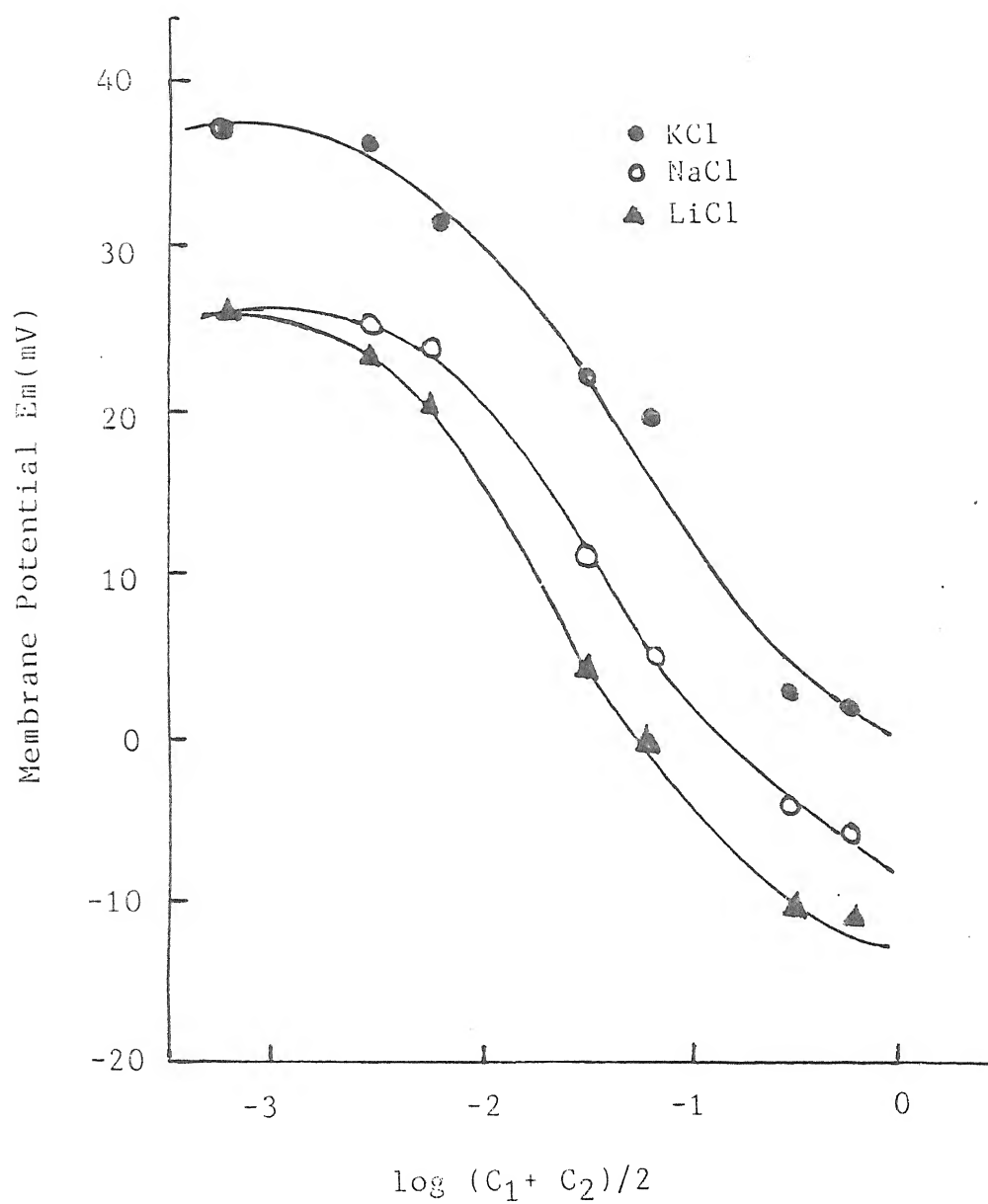
Fig.1.2. Plots of membrane potentials Em(mV) against $\log(C_1 + C_2)/2$ using 1:1 electrolytes across nickel sulphide membrane.

TABLE 1.3

EXPERIMENTALLY OBSERVED VALUES OF MEMBRANE POTENTIAL E_m (mV)

ACROSS HEN EGG SHELL MEMBRANE IN CONTACT WITH VARIOUS 1:1

ELECTROLYTES AT 25 ± 0.1 °C

Membrane	Hen egg shell		
Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (M)			
1.0/0.1	-6.5	-16.2	-21.0
0.5/0.05	-8.9	-18.8	-20.5
0.1/0.01	-14.7	-24.0	-25.5
0.05/0.005	-16.2	-29.3	-32.0
0.01/0.001	-19.5	-33.5	-33.8
0.005/0.0005	-20.3	-34.8	-35.0
0.001/0.0001	-20.3	-34.8	-35.0

Vide Fig. 1.3
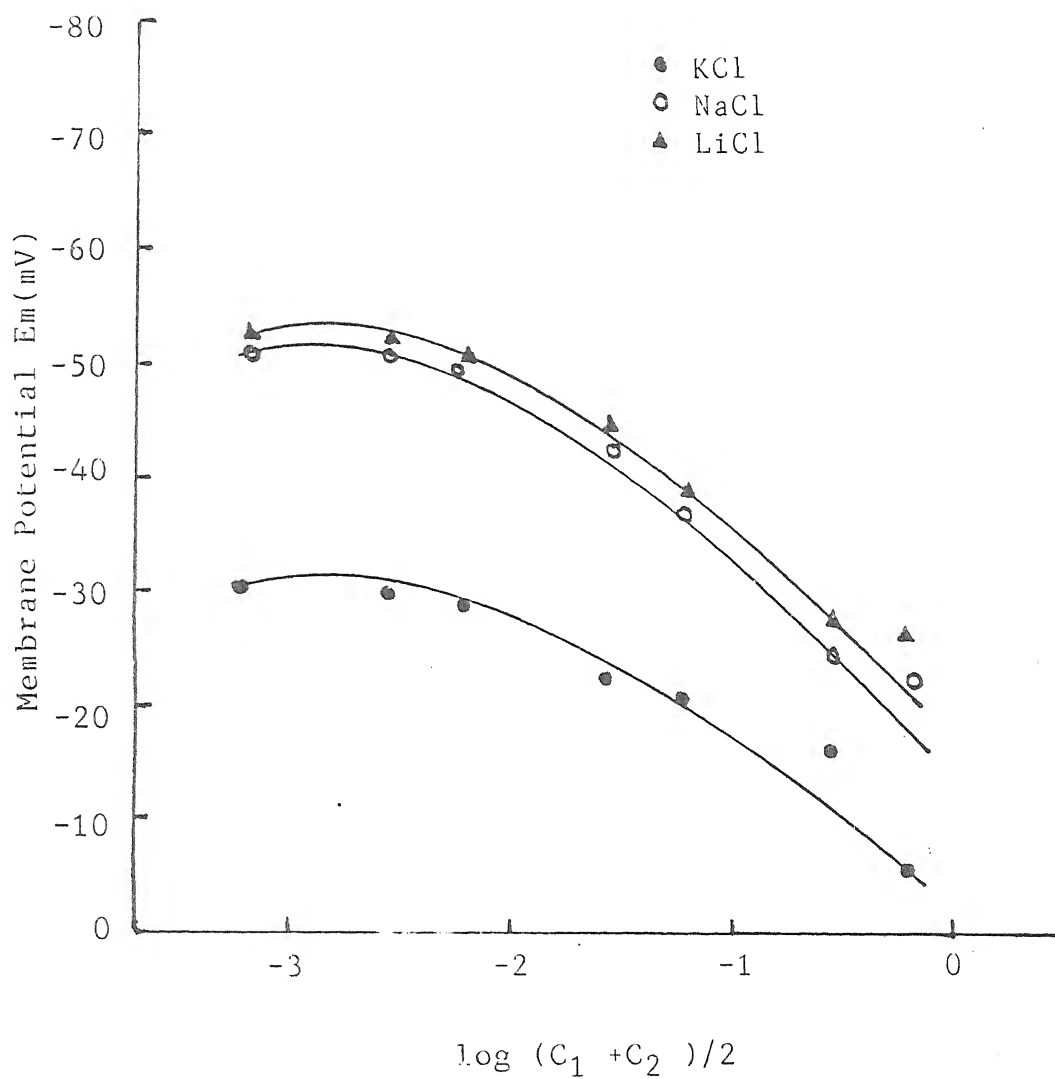
Fig.1.3. Plots of membrane potentials Em(mV) against log $(C_1+C_2)/2$ using 1:1 electrolytes across hen egg shell membrane

little charge on it can give ideal potentials according to the Nernst equation.

$$E = (RT/F) \ln a_1/a_2 \qquad (1.1)$$

Where a_1 and a_2 are the activities of the two solutions on either side of the membrane, E is the membrane potential and R, T and F have their usual meanings.

The values of membrane potential E_m (mV) observed across mercuric and nickel sulphide membranes are positive when the membranes are used to separate dilute solutions (dilute solution side taken as positive).The values are low when the membranes are used to separate concentrated solution of an electrolyte whereas it increases as the solutions are diluted and reach to a maximum value this means these parchment supported membranes are negatively charged (cation selective) and selectivity increases with dilution. The negative charge may be attributed to the preferential adsorption of hydroxyl ions from water and, or sulphide ions present in the solution used for the preparation of the membranes.

Two important factors which control electrolyte permeability through a membrane are charge on the membrane and its porosity. Parchment paper, except for the presence of some stray and end Carboxylic group, Contains very few fixed groups. Deposition of inorganic precipitate gives rise to a net negative charge on membrane surface in the dilute solutions of a 1:1 electrolyte leading to the type of ionic distribution associated with the

electrical double layer (25). The stepwise change in membrane potential or the selectivity character of the membrane-electrolyte system may readily be explained in terms of the structural changes produced in the electrical double layer at the interfaces.

In hen egg shell membrane the commonest substance due to which the membrane is composed is Keratin. Though this protein seems to take many forms and to have exactly the same properties in different solutions (34-37). According to Kitchava et al.(38)the outer layer of the egg vitelline membrane consisted of polypeptides showing mostly and α-helix structure, whereas the inner layer mainly contained peptides with randomcoil structure. Very little is known about the relative proportions of yolk,white and the shell membrane in the egg of lower animals, although the minerological and morphological structure of shell is well under-stood (36).

An interesting point with the values of E_m is the fact that these are negative in all the electrolyte concentr-ation ranges. However, the values of E_m decrease algebraically as the electrolyte concentration across the membrane is increased. This means that the membrane in contact with dilute electrolyte solutions is anion selective whereas the anion selectivity decre-ases as the concentration across the membrne is increased. The egg shell membrane is considered to be negatively charged in contact with water. It is quite probable that in these cases

the negative charge is due to the firm attachment of hydroxide ions from water and few inorganic groups of organic fibers (37) constituting the egg shell membrane. An equivalent number of protones and/or cations, some closely held in the fixed part of the double layer and the remainder in the diffused portion, is left in the solution. By the addition of uni-univalent electroly- tes, there will be a tendency for cations to accumulate on the solution side of the fixed double layer by increasing the positi- ve charge density, the interfacial potential difference changed thereby changing the overall membrane potential and the membrane becomes less selective. If the electrolyte concentrations are further increased the overall membrane potential or the selectiv- ity character of the membrane changes.

The fixed groups present in well characterized ionexchange membranes can be easily estimated by titration. This procedure was used by sollner (39) to estimate the end groups and stray Carboxylic groups present in the collodion material. Lakshminarayanaiah (40) in his studies with thin membranes of parlodion, used two methods the isotopic and the potentiometric to evaluate the apparent fixed charge on the membrane material.In the present studies the titration method proved inconvenient and very inaccurate, while the isotopic method was described in view of the strong ionic adsorption phenomena exhibited by these systems. Consiquently the potentiometric method based on fixed charge theory of membrane potential has been used for the evalua-

tion of effective fixed charge density of mercuric, nickel sul-
phide parchment supported membranes and hen egg shell biological
membrane.

The fixed charge concept of Teorell (2,3), Meyer and
Sievers (4) (TMS theory) for charged membranes is a partinent
starting point for the investigation of the actual mechanisms of
the ionic or molecular processes which occur in the membrane pha-
se. According to this theory membrane potential is considered to
be composed of two Donnan potential at the two solution-membrane
interfaces and a diffusion potential arising from unequal concen-
tration of the two membrane phases. These authors derived follow-
ing equation for membrane potential in millivolts (at $25^{\circ}C$)
applicable to a highly idealized system, viz:

$$E_m = 59.2 \left[\log \frac{C_2(\sqrt{4C_1^2+\overline{X}^2}+\overline{X})}{C_1(\sqrt{4C_2^2+\overline{X}^2}+\overline{X})} + \overline{U} \log \frac{\sqrt{4C_2^2+\overline{X}^2}+\overline{X}\overline{U}}{\sqrt{4C_1^2+\overline{X}^2}+\overline{X}\overline{U}} \right] \quad (1.2)$$

where $\overline{U}=(\overline{u}-\overline{v})/(\overline{u}+\overline{v})$, $\overline{u}$ and $\overline{v}$ are the mobilities of cation and
anion respectively in the membrane phase; $\overline{X}$ is the charge on the
membrane expressed in equivalents/litre of imbibed solution.
Equation (1.2) has been frequently used for the evaluation of the
fixed charge density $\overline{X}$ of a membrane (41). In order to evalute
this parameter for the simple case of 1:1 electrolyte and mem-
brane carrying a net charge of unity ($\overline{X} = \pm 1$),theoritical concen-
tration potentials E_m existing across the membrane were calculat-

ed as a function of log C_2, are given in Table 1.4 and 1.5. The ratio (C_2/C_1) being kept at constant value of 10 for different mobility ratios, $\overline{u}/\overline{v}$ and plotted as shown in Figs.,(1.4-1.6). The observed membrane potential values using various 1:1 electrolyte are plotted in the same graph as a function of log $1/C_2$. The experimental curve is shifted horizontally until it coincides with one of the theoritical curves. The extent of this shift gives log $\overline{X}$ and the coinciding theoritical curve gave the value for $\overline{u}/\overline{v}$, Figs. (1.4-1.6). The observed membrane potential values for mercuric and nickel sulphide parchement supported membranes were plotted in the Fig. (1.4) and (1.5) respectively, while for hen egg shell membrane these are plotted in Fig. (1.6). The values of $\overline{X}$ and $\overline{u}/\overline{v}$ derived in this way for all the three membranes with various 1:1 electrolytes combinations are given in Table 1.6. It is, however, noted that the experimental curves for hen egg shell membrane after shifting horizontally did not overlap completely with any of the horizontal curves in all the electrolyte concentration ranges studied. This discrepency is not peculiar for nickel and mercuric sulphide membranes as well as for other systems (27-29,42-44). Hen egg shell membrane has the similar nature of observed membrane potential as the potential measured across duramater, the membrane surrounding the brain of buffalo (45) and the peritoneal membrane (46).

Kobatake et al.(47) on the basis of the thermodynamics of irreversible processes derived the following equation for the

TABLE 1.4

THEORITICAL VALUES OF MEMBRANE POTENTIALS E $_m$ (mV) CALCULATED FROM

TEORELL-MEYER-SIEVERS METHOD FOR DIFFERENT MOBILITY RATIO $\overline{u} / \overline{v}$

AND $(\overline{X}=1)$ AT DIFFERENT CONCENTRATIONS

Mobility ratio $\overline{u} / \overline{v}$	0.2	0.4	0.6	0.8	1.0	1.2
Concentration C_2/C_1 (M)						
1.0/0.1	15.0	30.0	45.2	46.0	45.0	34.0
0.5/0.05	35.0	40.0	47.5	47.0	50.2	50.0
0.1/0.01	50.0	50.0	50.0	55.5	55.0	55.0
0.05/0.005	58.0	57.0	55.0	58.0	59.0	59.0
0.01/0.001	59.0	59.0	59.0	59.0	59.9	59.9
0.005/0.0005	60.0	60.0	60.0	60.0	60.0	60.0
0.001/0.0001	60.00	60.0	60.0	60.0	60.0	60.0

Vide Figs. 1.4-1.5
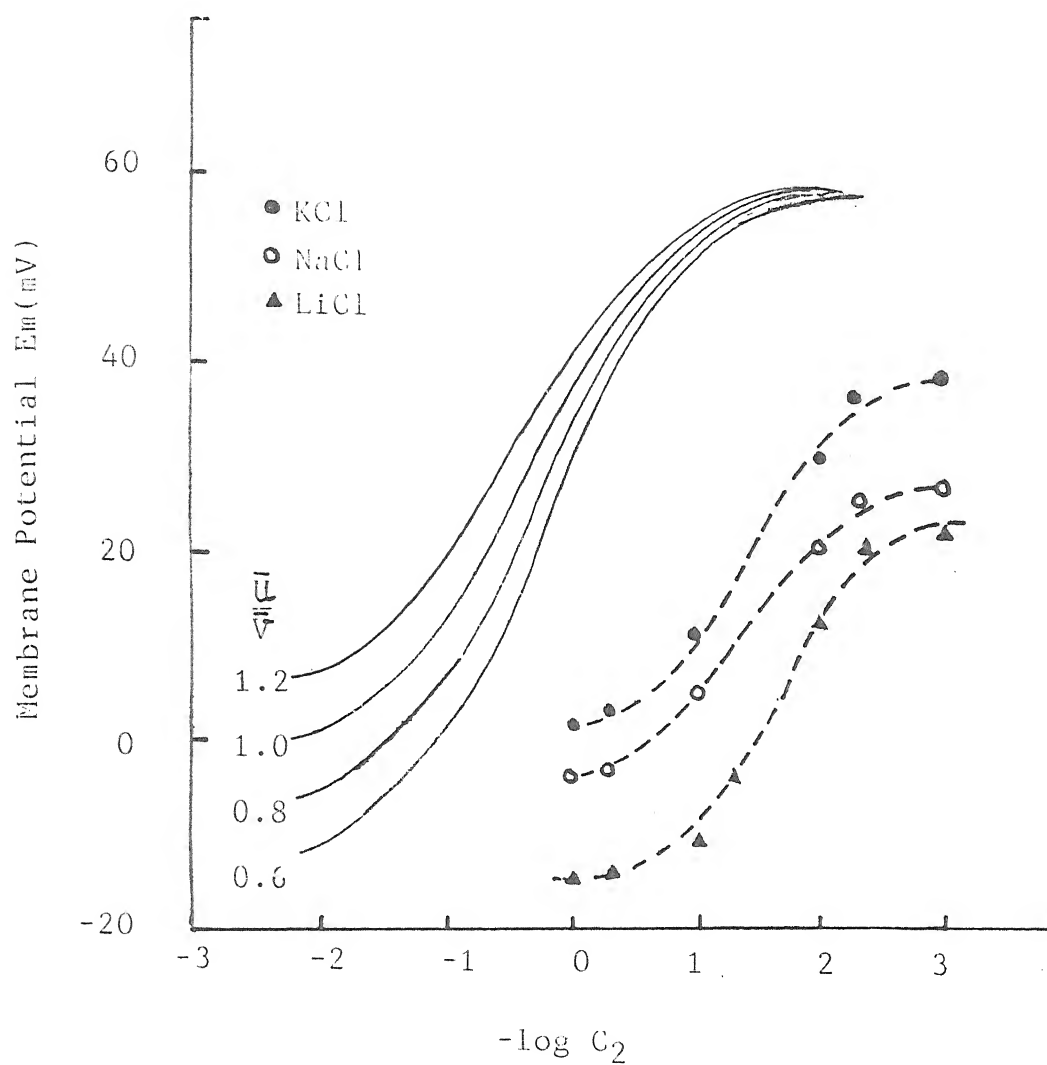
Fig.1.4. Plots of membrane potentials Em Vs.log1/C_2 for mercuric sulphide membrane in contact with various 1:1 electrolytes.
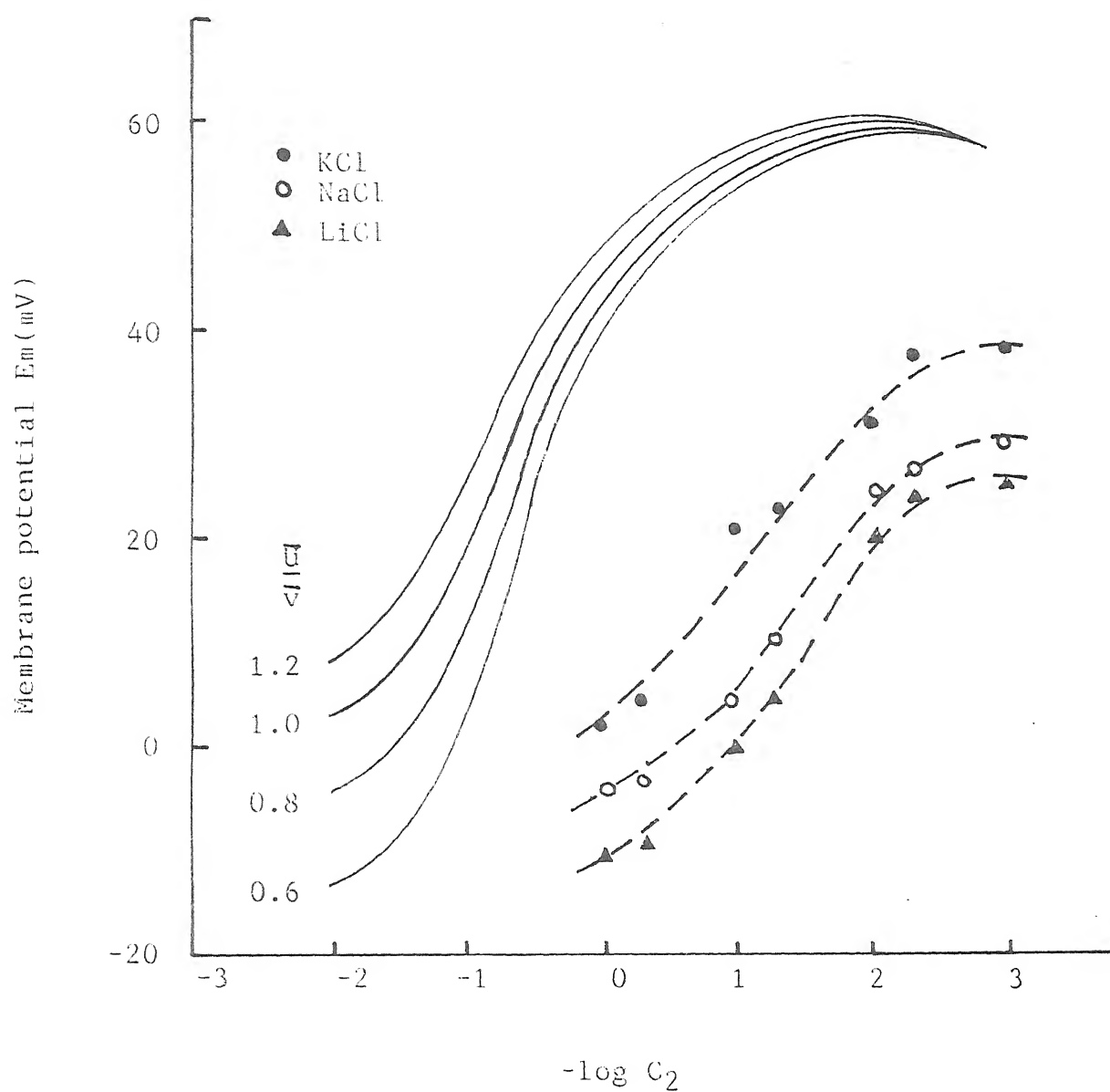
Fig.1.5. Plots of membrane potentials Em Vs. log $1/C_2$ for nickel sulphide membrane in contact with various 1:1 electrolytes.

TABLE 1.5

THEORITICAL VALUES OF MEMBRANE POTENTIALS E_m (mV) CALCULATED FROM

TEORELL-MEYER-SIEVERS METHOD FOR DIFFERENT MOBILITY RATIO $\bar{u} / \bar{v}$

AND ($\bar{X}$=-1) AT DIFFERENT CONCENTRATIONS

Mobility ratio $\bar{u} / \bar{v}$	0.4	0.5	0.6	0.7	0.8	0.9
Concentration C_2/C_1 (M)						
1.0/0.1	-9.1	-12.5	-16.2	-18.5	-21.1	-23.3
0.5/0.05	-11.5	-15.3	-18.7	-20.2	-23.0	-25.4
0.1/0.01	-15.5	-18.2	-21.0	-23.5	-26.5	-28.6
0.05/0.005	-22.7	-22.8	-25.4	-27.6	-30.1	-32.3
0.01/0.0001	-30.0	-32.5	-35.0	-37.0	-38.2	-38.3
0.005/0.0005	-37.1	-43.1	-46.2	-47.1	-48.1	-47.9
0.001/0.0001	-54.0	-54.1	-54.2	-54.4	-54.4	-54.5

Vide Fig. 1.6
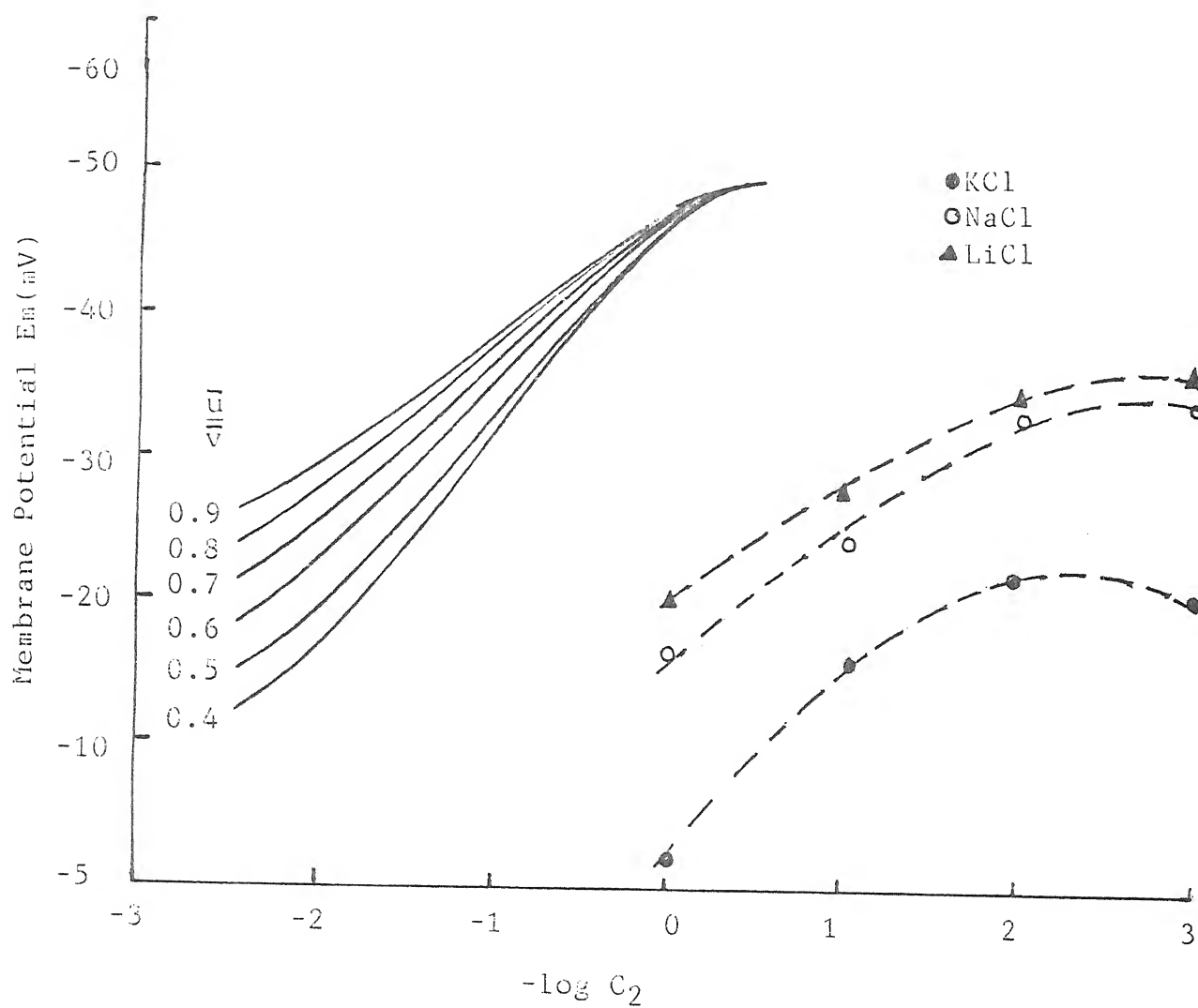
Fig.1.6. Plots of membrane potentials Em Vs. $\log \cdot 1/C_2$ for hen egg shell membrane in contact with various 1:1 electrolytes.

TABLE 1.6

VALUES OF EFFECTIVE FIXED CHARGE DENSITY $\overline{X}$ (eq/1) AND MOBILITY RATIO ($\overline{u}/\overline{v}$) FOR VARIOUS MEMBRANE ELECTROLYTE SYSTEMS USING TMS METHOD AT 25 ± 0.1 $^{\circ}$C

Electrolyte		KCl	NaCl	LiCl
Membranes	Parameters			
Mercuric sulphide	$(\overline{X})\times10^2$	3.5	1.6	4.7
	$(\overline{u}/\overline{v})$	1.0	0.8	0.6
Nickel sulphide	$(\overline{X})\times10^2$	2.3	1.6	2.2
	$(\overline{u}/\overline{v})$	0.8	0.6	0.8
Hen egg shell	$(\overline{X})\times10^2$	2.5	4.0	4.6
	$(\overline{u}/\overline{v})$	0.9	0.7	0.5

electrical potential E_m which arises when a negatively charged membrne separates two solutions of a 1:1 electrolyte of concentrations C_1 and C_2 ($C_1 < C_2$):

$$E_m = - \frac{RT}{F} \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - (1 + \frac{1}{\beta} - 2\alpha) \ln \left(\frac{C_2 + \alpha\beta\overline{X}}{C_1 + \alpha\beta\overline{X}} \right) \right]$$

(1.3)

where $\alpha = U/(u+v)$

$\beta = 1 + KF\overline{X}/u$

F and K represent, respectively, the faraday constant and a constant dependent upon the viscosity of the solution and structural details of the polymer network of which the membrane is composed. To evaluate the membrane parameters, α, β and $\overline{X}$, two limiting forms of the above equation were derived. When the external salt concentration C is sufficiently small,

$|E^{\sigma}_m| = (1/\beta) \ln\tau - (\tau - 1/\alpha\beta\tau)(1 + 1/\beta - 2\alpha)(C_2/\overline{X}) + \ldots (1.4)$

where $|E^{\sigma}_m| = F(E_m/RT)$

and $\tau = C_2/C_1$

when the salt concentration C is high,

$1/t_- = (1/1-\alpha) + [(1+\beta-2\alpha\beta)(\tau-1)\alpha / 2(1-\alpha)^2 \ln\tau](\overline{X}/C_2) + \ldots (1.5)$

Where t_- is the apparent transference number of coions (anions) in a negatively charged membrane defined by

$|E^{\sigma}_m| = (1-2t_-) \ln\tau$ (1.6)

The values of t_- calculated from observed membrane potentials using eq. (1.6) for mercuric and nickel sulphide parchment supported membranes and hen egg shell biological membrne

electrical potential E_m which arises when a negatively charged membrne separates two solutions of a 1:1 electrolyte of concentrations C_1 and C_2 ($C_1 < C_2$):

$$E_m = - \frac{RT}{F} \left[\frac{1}{\beta} \ln \frac{C_2}{C_1} - (1 + \frac{1}{\beta} - 2\alpha) \ln \left(\frac{C_2 + \alpha\beta\overline{X}}{C_1 + \alpha\beta\overline{X}} \right) \right]$$

(1.3)

where $\alpha = U/(u+v)$

$\beta = 1 + KF\overline{X}/u$

F and K represent, respectively, the faraday constant and a constant dependent upon the viscosity of the solution and structural details of the polymer network of which the membrane is composed. To evaluate the membrane parameters, α, β and $\overline{X}$, two limiting forms of the above equation were derived. When the external salt concentration C is sufficiently small,

$|E^{\sigma}_m| = (1/\beta) \ln\tau - (\tau - 1/\alpha\beta\tau) (1 + 1/\beta - 2\alpha) (C_2/\overline{X}) + \ldots$ (1.4)

where $|E^{\sigma}_m| = F (E_m/RT)$

and $\tau = C_2/C_1$

when the salt concentration C is high,

$1/t_- = (1/1-\alpha) + [(1 + \beta - 2\alpha\beta) (\tau - 1)\alpha / 2(1-\alpha)^2 \ln\tau] (\overline{X}/C_2) + \ldots$ (1.5)

Where t_- is the apparent transference number of coions (anions) in a negatively charged membrane defined by

$|E^{\sigma}_m| = (1 - 2t_-) \ln\tau$ (1.6)

The values of t_- calculated from observed membrane potentials using eq. (1.6) for mercuric and nickel sulphide parchment supported membranes and hen egg shell biological membrne

are given in Tables 1.7-1.9. Equation (1.4) was used to give the value of β (see Table 1.10) and a relation between α and $\overline{X}$ by evaluating the intercept and the initial slope of the plot of $|E^{\sigma}_m|$ against C_2 (Figs. 1.7-1.9), while eq. (1.5) was used to evaluate α (see Table 1.10) from the intercept of a plot of $1/t_-$ against $1/C_2$ (Figs. 1.10-1.12). The values of $\overline{X}$ were determined by inserting this value of α in the relation between α and $\overline{X}$ obtained earlier. The values of $\overline{X}$ derived in this way for the membranes and 1:1 electrolytes are given in Table 1.11.

Once the values of the parameters α, β and $\overline{X}$ for a given membrane-electrolyte system have been determined one can get the theoretical E_m using eq. (1.3) and compare it with the corresponding experimental data. For this comparison eq. (1.3) can be rewritten in the following form as suggested by Kobatake and co-workers (47).

$$(\tau - e^q)/(e^q - 1) = Z \qquad (1.7)$$

with q and z defined by

$$q = |E^{\sigma}_m| + (1-2\alpha)\ln\tau \; / \; 1/\beta + (1-2\alpha)$$

and $z = C_2/\alpha\beta\overline{X}$. Thus if eq. (1.7) is valid, the value of $(\tau - e^q)/(e^q - 1)$ calculated from the measured E_m with predetermined α, β and $\overline{X}$ and the given value of τ must fall on a straight line which has a unit slope and passes the co-ordinate origin when plotted against z. this vehaviour should be observed irrespective of the value of τ and the kind of membrane-electrolyte system used.Figs.(1.13-1.15) demonstrate that the theoritical
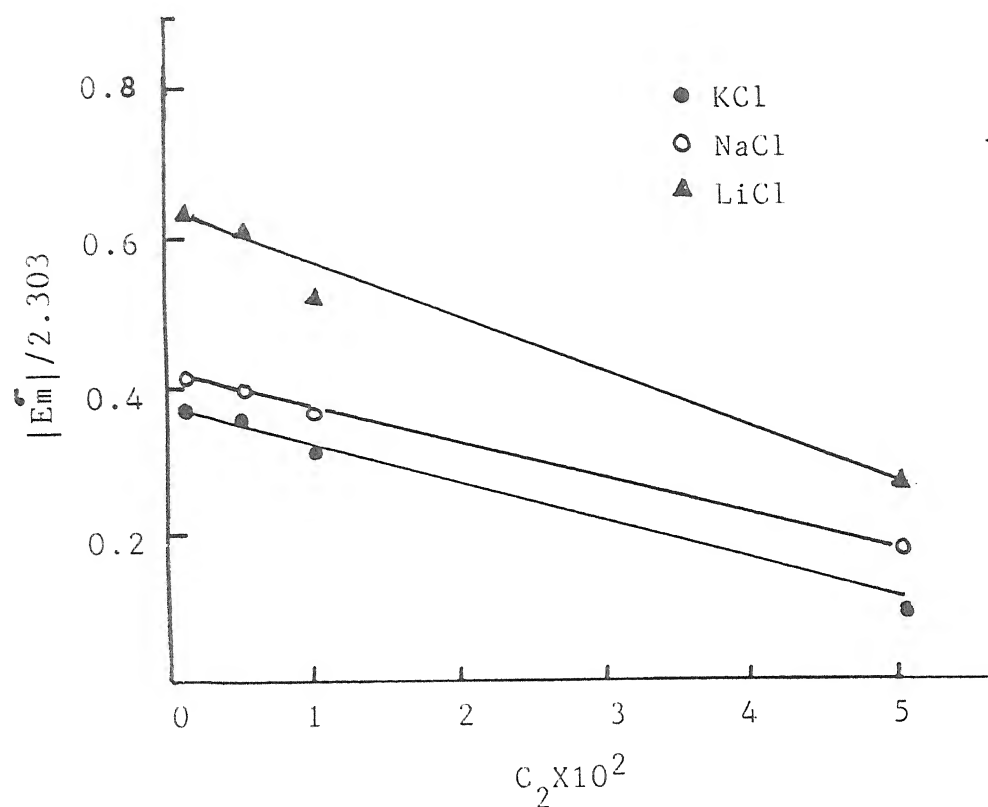
Fig.1.7. Plots of $|E_m|/2.303$ against $C_2 X 10^2$ for mercuric sulphide membrane in contact with various 1:1 electrolyte solutions.
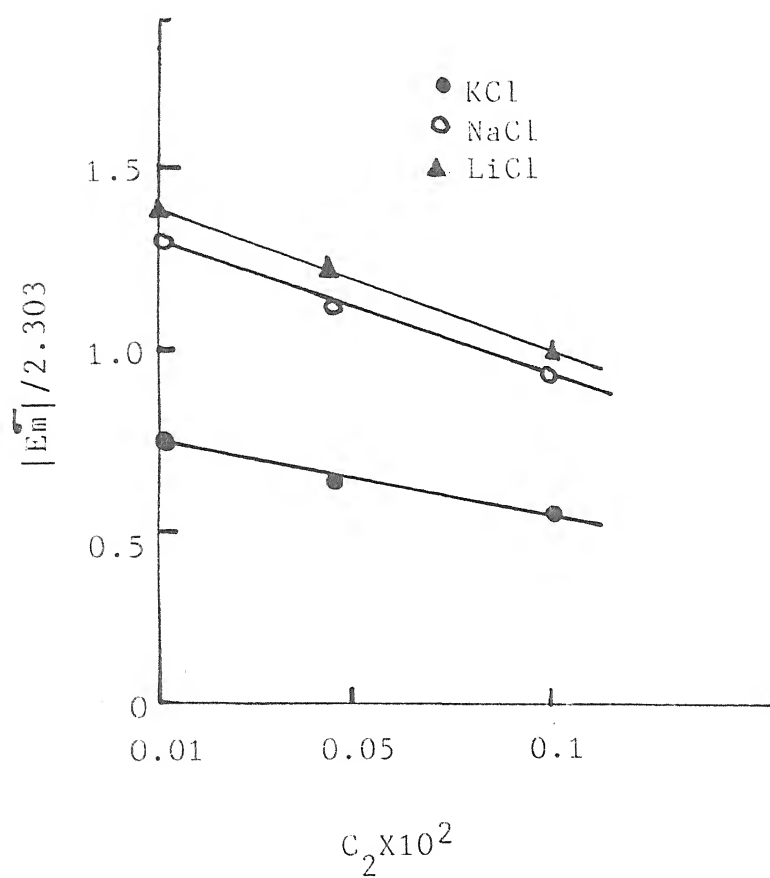
Fig.1.9. Plots of $|\widehat{Em}|/2.303$ against $C_2 \times 10^2$ for hen egg shell membrane in contact with various 1:1 electrolyte solutions.

TABLE 1.7

TRANSFERENCE NUMBER t_- OF COIONS (ANIONS) DERIVED FROM OBSERVED MEMBRANE POTENTIAL AT VARIOUS ELECTROLYTE CONCENTRATIONS THROUGH MERCURIC SULPHIDE MEMBRANE

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (M)			
1.0/0.1	0.49	0.53	0.63
0.5/0.05	0.48	0.53	0.62
0.1/0.01	0.40	0.45	0.61
0.05/0.005	0.36	0.41	0.55
0.01/0.001	0.26	0.37	0.35
0.005/0.0005	0.20	0.31	0.32
0.001/0.0001	0.19	0.30	0.32

Vide Fig. 1.10
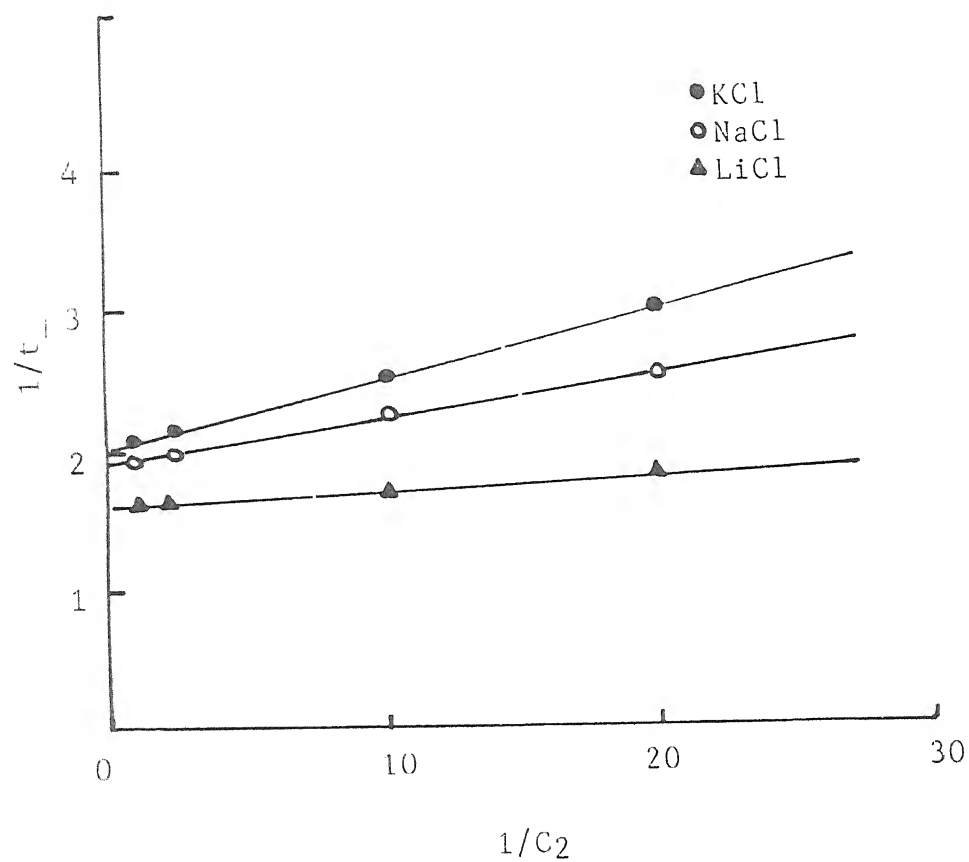
Fig.1.10. Plots of $1/t_-$ against $1/C_2$ for mercuric sulphide membrane using 1:1 electrolyte solutions at constant γ (γ=10).

TABLE 1.8

TRANSFERENCE NUMBER t_ OF COIONS (ANIONS) DERIVED FROM OBSERVED
MEMBRANE POTENTIAL AT VARIOUS ELECTROLYTE CONCENTRATIONS THROUGH
NICKEL SULPHIDE MEMBRANE

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (M)			
1.0/0.1	0.48	0.55	0.59
0.5/0.05	0.47	0.53	0.59
0.1/0.01	0.33	0.45	0.50
0.05/0.005	0.31	0.41	0.45
0.01/0.001	0.24	0.30	0.39
0.005/0.0005	0.19	0.29	0.29
0.001/0.0001	0.18	0.28	0.28

Vide Fig. 1.11
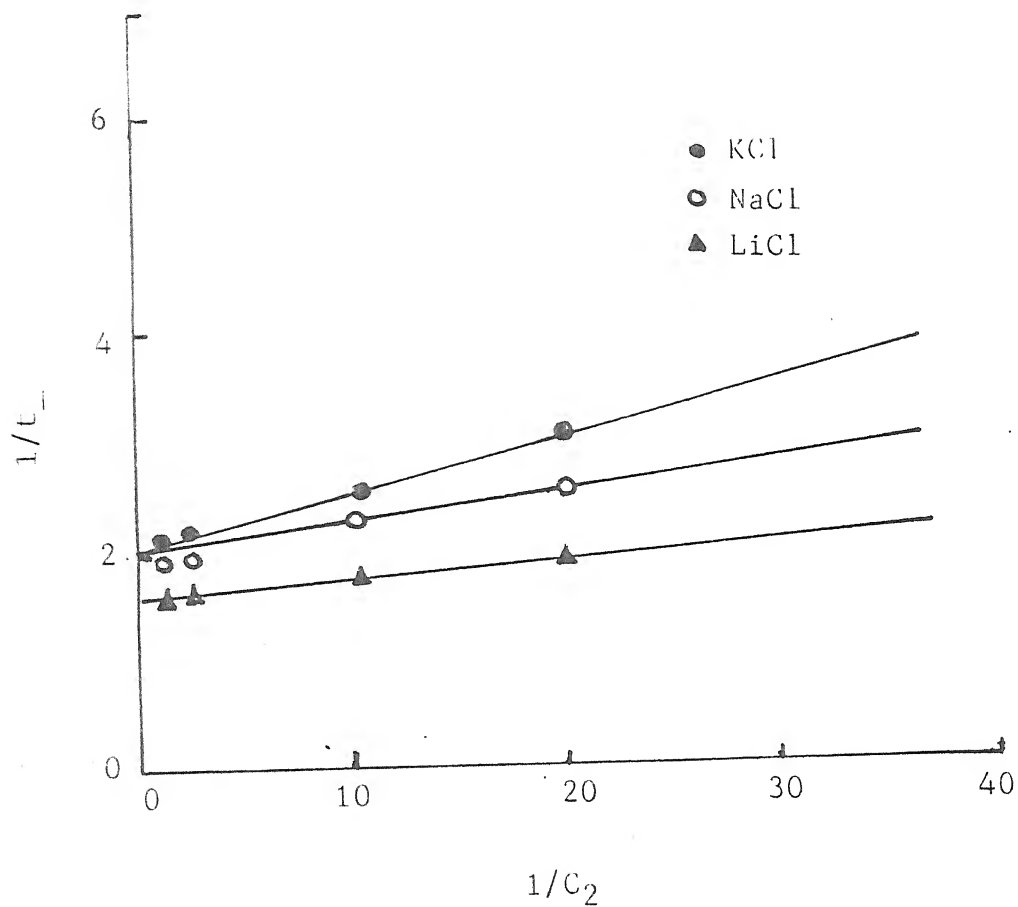
Fig.1.11. Plots of $1/t_-$ against $1/C_2$ for nickel sulphide membrane using 1:1 electrolyte solutions at constant γ ($\gamma = 10$).

TABLE 1.9

TRANSFERENCE NUMBER t̲ OF COIONS (ANIONS) DERIVED FROM OBSERVED
MEMBRANE POTENTIAL AT VARIOUS ELECTROLYTE CONCENTRATIONS THROUGH
HEN EGG SHELL MEMBRANE

Membrane	Hen egg shell		
Electrolyte	KCl	NaCl	LiCl
Concentration C_2/C_1 (M)			
1.0/0.1	0.45	0.36	0.33
0.5/0.05	0.43	0.34	0.32
0.1/0.01	0.38	0.30	0.28
0.05/0.005	0.36	0.25	0.23
0.01/0.001	0.34	0.22	0.21
0.005/0.0005	0.32	0.21	0.20
0.001/0.0001	0.31	0.21	0.18

Vide Fig. 1.12
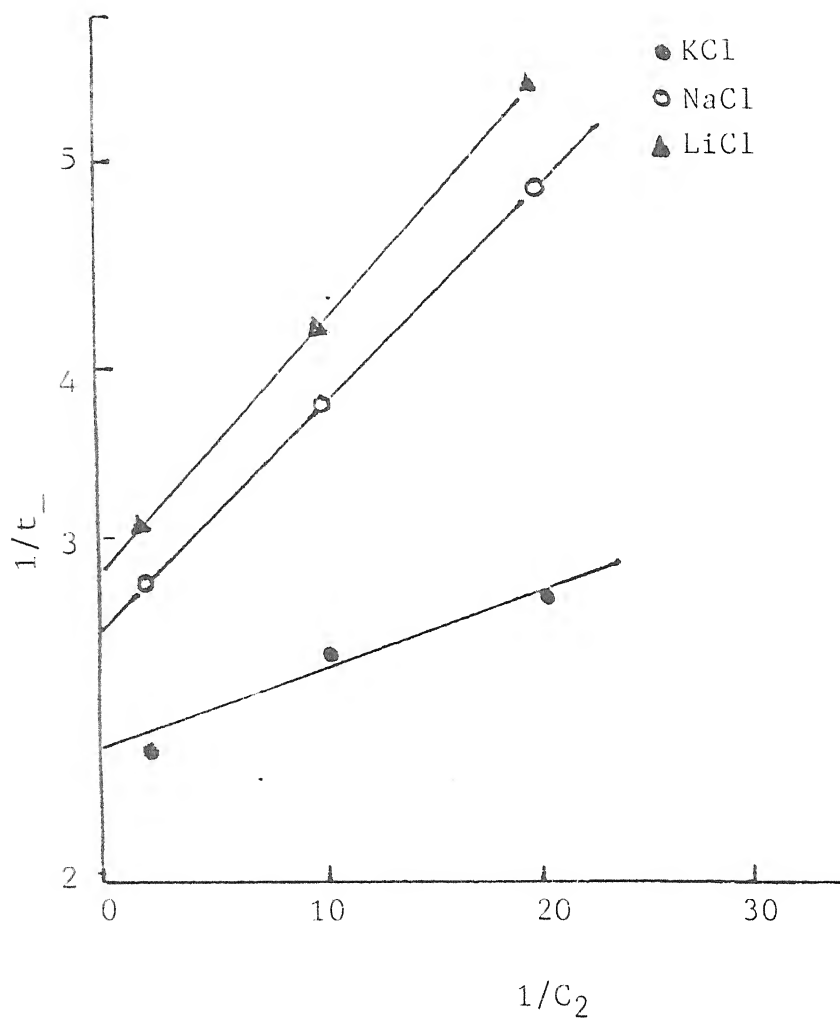
Fig.1.12. Plots of 1/t_ against 1/C$_2$ for hen egg shell membrane using 1:1 electrolyte solutions at constant γ (γ=10).

TABLE 1.10

VALUES OF THE MEMBRANE PARAMETERS α AND β FOR VARIOUS MEMBRANE ELECTROLYTES SYSTEMS AT τ=10.

Electrolyte	KCl		NaCl		LiCl	
Membranes	α	β	α	β	α	β
Mercuric sulphide	0.51	1.5	0.44	2.3	0.38	2.7
Nickel sulphide	0.50	1.6	0.44	2.4	0.37	2.7
Hen egg shell	0.58	3.07	0.63	1.7	0.67	1.6

TABLE 1.11

VALUES OF EFFECTIVE FIXED CHARGE DENSITIES OF MERCURIC SULPHIDE,
NICKEL SULPHIDE AND HEN EGG SHELL MEMBRANES USING VARIOUS 1:1
ELECTROLYTES DERIVED FROM DIFFERENT THEORIES

Membrane	Mercuric sulphide			Nickel sulphide			Hen egg shell		
Electrolyte	KCl	NaCl	LiCl	KCl	NaCl	LiCl	KCl	NaCl	LiCl
TMS									
$(\overline{X}) \times 10^2$ (eqn/1) equqtion (1.2)	3.5	1.6	4.7	1.8	1.4	2.5	2.5	4.0	4.6
Kobatake et al.									
$(\overline{X}) \times 10^2$ (eqn/1) equation (1.4)	4.3	1.5	3.0	2.3	1.8	2.5	3.5	6.2	6.1
Tasaka et al.									
$(\emptyset X) \times 10^2$ (eqn/1) equation (1.10)	1.9	0.99	1.9	2.8	1.4	1.5	3.6	5.2	5.4

Fig.1.13. Plots of $\log(\gamma - e^q)/(e^q-1)$ against log Z for mercuric sulphide membrane in contact with various 1:1 electrolytes.
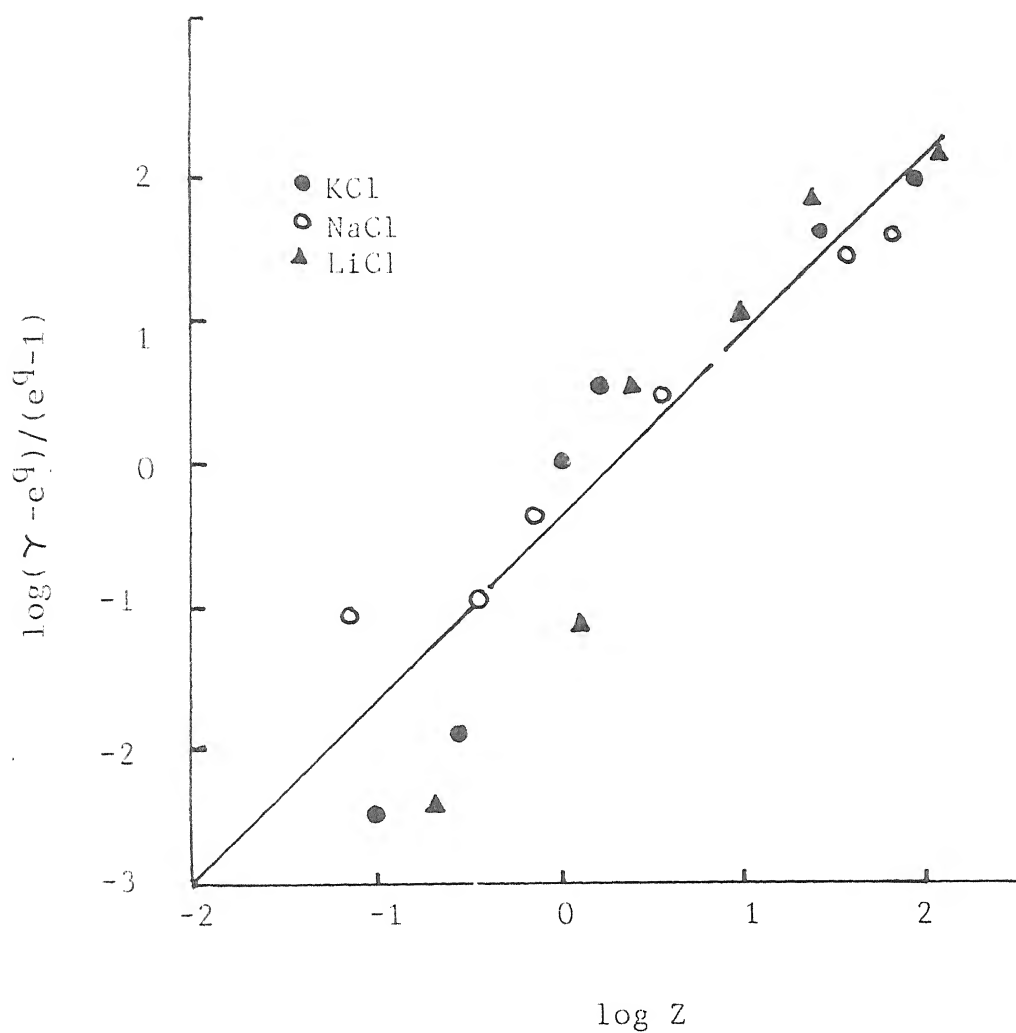
Fig.1.14. Plots of $\log(\gamma - e^q)/(e^q - 1)$ against $\log Z$ for nickel sulphide membrane in contact with various 1:1 electrolytes.
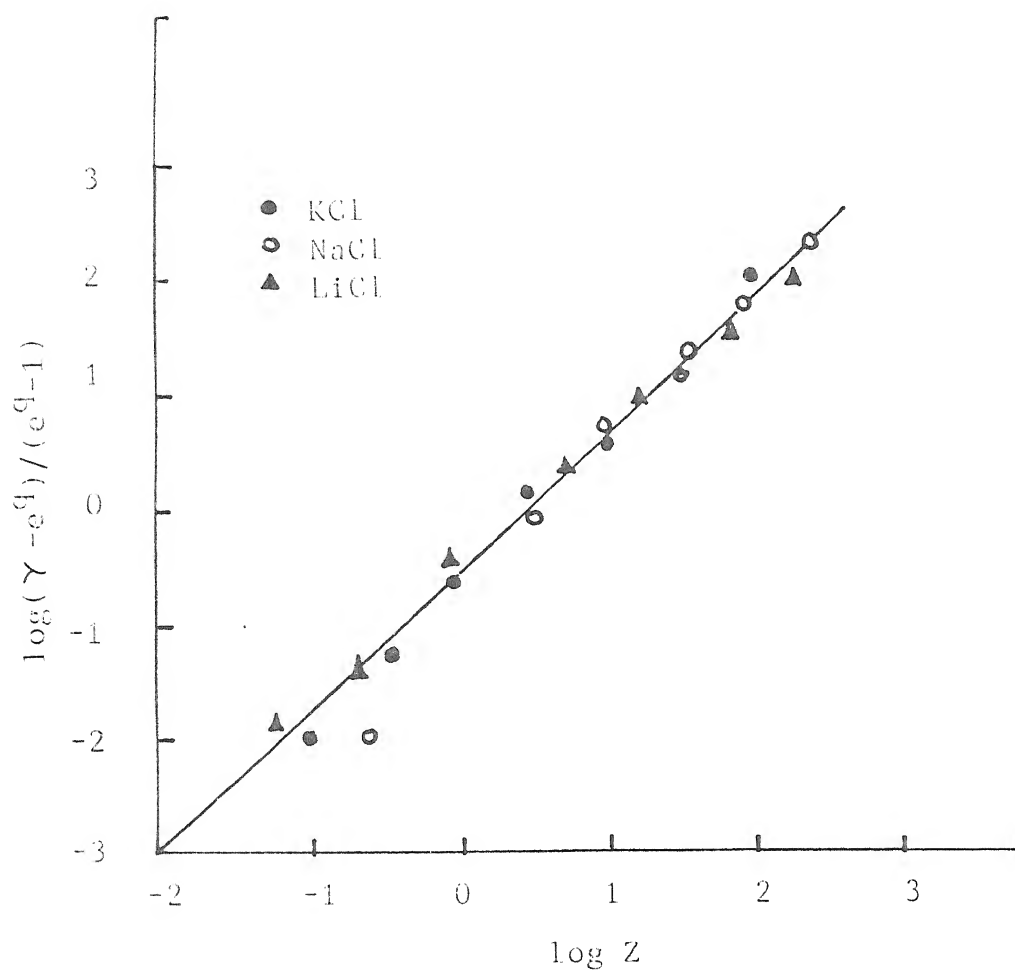
Fig.1.15. Plots of $\log(\gamma - e^q)/(e^q - 1)$ against $\log Z$ for hen egg shell membrane in contact with various 1:1 electrolytes.

prediction of eq.(1.7) [or eq.(1.3)] is borne out quite satisfactory by our experimental results on parchment supported mercuric and nickel sulphide membranes and hen egg shell membrane respectively.

Tasaka et al.(22) derived an equation for the membrane potential existing across a charged membrane. The total membrane potential E_m was considered as the sum of a diffusion potential E_d inside the membrane and the electrostatic potential differences E_e between the membrane surfaces and the electrolyte solutions on both sides of the membrane. The diffusion potential E_d was obtained by integrating the basic flow equation for diffusion (48) while the electrostatic potential difference was calculated from the Donnan's theory, Stated mathematically.

$$E_m = E_d + E_e \qquad (1.8\ a)$$

where

$$-E_d = -\int_1^2 \frac{J_o}{F\bar{C}_o} \frac{\emptyset X}{(\bar{C}+\emptyset X)u + \bar{C}v}\, dx + \frac{RT}{F} \int_1^2 \frac{(\bar{C}+\emptyset X)u}{(\bar{C}+\emptyset X)u + \bar{C}v}\, d\ln\bar{a}_+$$

$$- \frac{RT}{F} \int_1^2 \frac{\bar{C}v}{(\bar{C}+\emptyset X)u + \bar{C}v}\, d\ln\bar{a}_- \qquad (1.8\ b)$$

and

$$-E_e = -(RT/F)\ln(\bar{a}_1^- a_2^-/a_1^- \bar{a}_2^-) \qquad (1.8\ c)$$

where a_1^- and a_2^- are the activities of the electrolytes on the two sides of the membrane, the overbar refers to the phenomena in the membrane phase. J_o is the flow of electrolyte in the absence of an external electric field, the other symbols have their usual significance. On integrating eq. (1.8) in the limit of high

electrolyte concentrations across the membrane potential :

$$-E_m = \frac{RT}{F} \left(\frac{\varnothing X}{2}\right) \left(\frac{\tau-1}{\tau}\right) \frac{1}{C_2} + \frac{RT}{F} \left(\frac{u-v}{u+v}\right)$$

$$\left[\{ 1 - \frac{\varnothing X J_O}{RT\bar{C}_O(u-v)K} \} \right] \bigg/ \left[\{ 1 - \frac{\varnothing X J_O}{2RT\bar{C}_O vK} \} \right] \ln\tau + \frac{RT\varnothing X}{2Fuv} \left(\frac{J_O}{RT\bar{C}_O K}\right)^2$$

$$\left[\{ 1 - \frac{\varnothing X J_O(u+v)}{4RT\bar{C}_O uvK} \} \bigg/ \{ 1 - \frac{\varnothing X J_O}{2RT\bar{C}_O vK} \}^2 \right] (\tau-1)C_2 \qquad (1.9)$$

AT high electrolyte concentrations, eq. (1.9) can be approximated by

$$-E_m = \frac{RT}{F} \left(\frac{\tau-1}{\tau}\right) \left(\frac{\varnothing X}{2}\right) \cdot \frac{1}{C_2} + \ldots \qquad (1.10)$$

Equation (1.10) predicts a linear relationship between E_m and $1/C_2$ from which $\varnothing X$ can be calculated. Plots of $E_m /(\tau-1)/\tau$ versus $1/C_2$ for the membrnes are represented in Figs. (1.16-1.18). A set of straight lines in agreement with eq. (1.10) are obtained. The values of $\varnothing X$ derived from the slope of the lines are given in Table 1.11.

The values of fixed charge densities evaluated from the two developed theories of Kobatake et al. and Tasaka et al. are closer to those derived from the TMS theory-the theory most widely used to interpret data on biological systems. The values obtained for parchment supported mercuric and nickel sulphide membranes and hen egg shell membrane vary significantly,depending on the different methods used.It is thus concluded that values of effective fixed charge densities evaluated using the different theories characterize the membranes accurately.
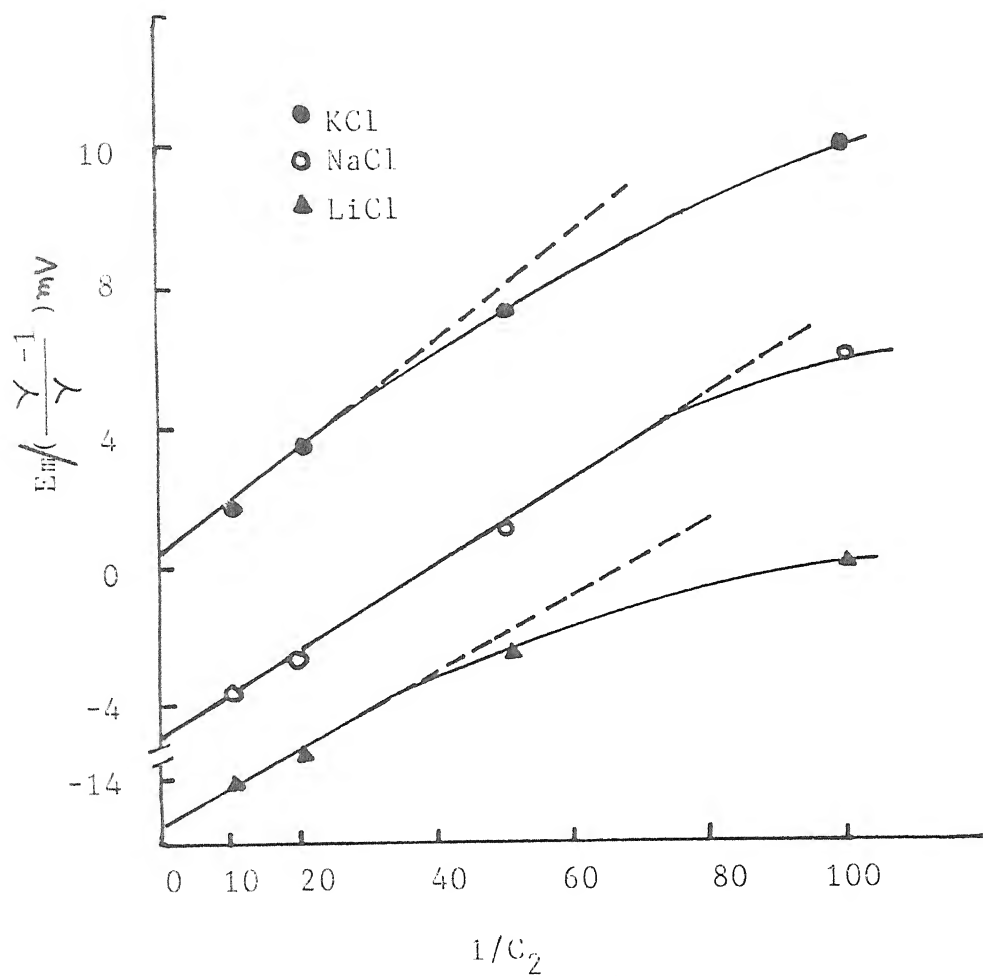
Fig.1.16. Plots of membrane potentials Em(mV) against $1/C_2$ for mercuric sulphide membrane in contact with various 1:1 electrolytes.
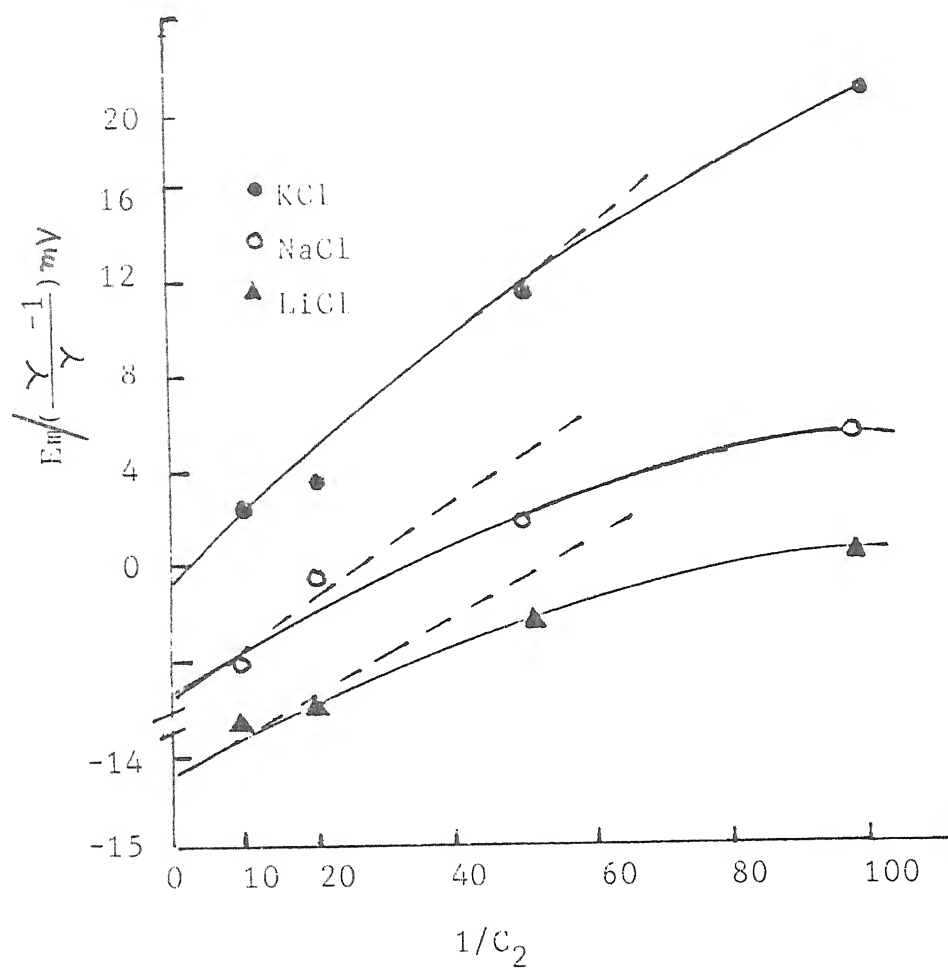
Fig.1.17 Plots of membrane potentials Em(mV)
against $1/C_2$ nickel sulphide membrane
in contact with various 1:1 electrolytes.
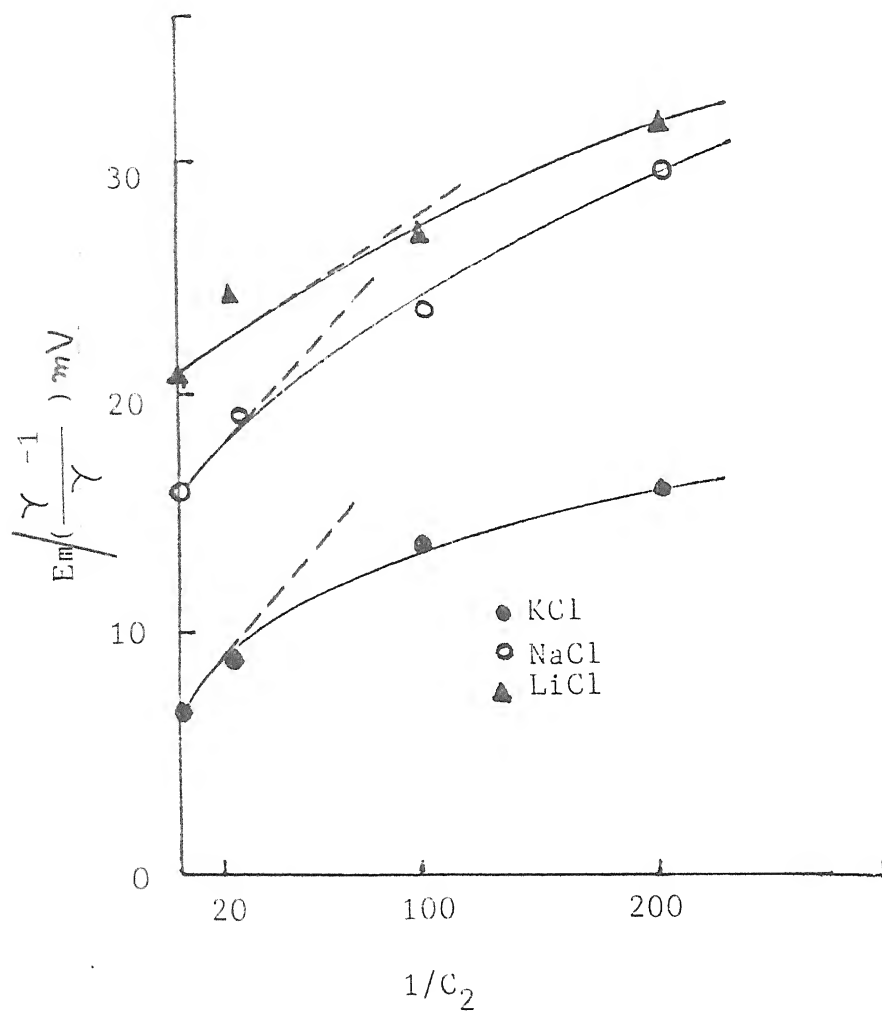
Fig.1.18. Plots of membrane potentials Em(mV) against $1/C_2$ for hen egg shell membrane in contact with various 1:1 electrolytes.

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CHAPTER-II
MEMBRANE SELECTIVITY

INTRODUCTION

The total electric potential difference observed under zero current flow between two aqueous solutions separeted by a membrane has been one of the most widely characterized electrochemical and bielectric phenomena (1-8). For biological membranes the eletrical potential difference is usually described in terms of Goldman-Hodgkin-Katz (9,10) equation whereas for certain ion exchange membranes permeable solely to species of one sign, it is described by a generalized Nernst equation. Both Goldman- Hodgkin-Katz and Nernst equations contain ionic permeability ratio terms. Depending on the transport mechanism or the assumption made in the derivation, the permeability ratio has been given various physical meanings as mobility ratio (11), ion exchange equilibrium constant (12), the product of the mobility ratio and the Donnan ratio (13,14), the product of the mobility ratio and the distribution coefficient ratio (10), the product of the mobility ratio and ion exchange equilibrium constant (15,16) or the product of the equivalent conductance ratio and the ratio of partition coefficients (17). Sandblom and Eisenman (17,1,18) have discussed the significance and implication of the observed permeability ratio. Recently a number of reviews have also been appeared dealing the ion selectivity of membranes (19-28).

In this chapter effective fixed charge density of the mercuric sulphide, nickel sulphide parchment supported membranes

and hen egg shell membrane has been used individually to calculate theoritical biionic potentials and compared with experemental determined values. The observed biionic potential values across the both parchment supported and egg shell membranes are used for the evaluation of membrane selectivity of ions. Membrane conductance values in contact with various 1:1 electrolytes have also been experimentally determined to substantiate our findings.

EXPERIMENTAL

The biionic potentials across freshly prepared mercuric and nickel sulphide membranes by the method of the interaction described earlier in chapter I and hen egg shell membrane was isolated from the freshly laid hen egg (29). Biionic potentials were determined by constructing electrochemical cell of the following type :

Hg-Hg$_2$Cl$_2$	Saturated KCl-Agar	Solution AX	Membrane	Solution BX	Saturated KCl-Agar	Hg-Hg$_2$Cl$_2$
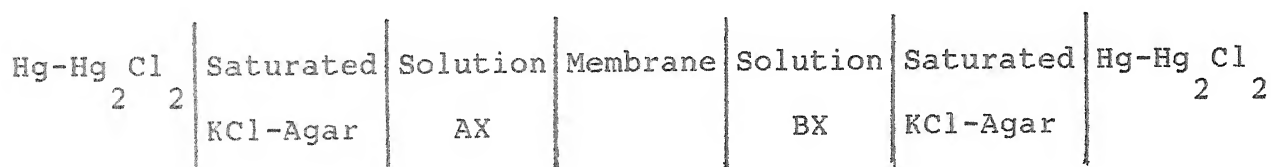
A pye-precision vernier potentiometer (No.7568) was used to observe the biionic potential values. Aqueous solution of sodium, potassium and lithium chlolrides (BDH,AR grade) were taken in the investigations. The solution on the both sides of the membrane were vigorously stirred with a pair of electrically operated magnetic stirrers to remove completely or at least to minimize the effect of film-control diffusion (30).

Electrical conductivity of the membrane was determined by setting up a cell of the type show in Fig. (2.1) with a conductivity bridge (Cambridge Instrument Company Ltd., England). All measurements were carried out at $25\pm0.1^{\circ}C$. The error in measurement of membrane potential was within 1.0% whereas the electrical conductance could be measured to better than 99.5% accuracy.

RESULTS AND DISCUSSION

When an ion exchange membrane of different concentraions is interposed between two solutions of an electrolyte the mobile species penetrate the membrane and various transport phenomena are introduced into the system (31). An electrical potential called a concentration or membrane potential is generated across the membrane. The sign and magnitude of this emf directs the selectivity of the membrane towards the ions of the electrolyte. If the membrane is used to separate the solution of the AX and BX (or AX and AY) type electrolytes, the steady potential developed is called biionic potential (32) which is a measure of the selectivity of the membrane for ions of the same sign. Biionic potential E_{BIP} has been considered by Helfferich (15), according to the concepts of the TMS theory,(13,14) as being the algebraic sum of two interfacial potentials and an internal diffusion potential. A complete mathematical discussion under conditions of (a) membrane diffusion control,(b) film diffusion control, and (c) coupled membrane film diffusion control, has been presented. For a general case that involves complete membrane diffusion control the

Conductivity Bridge

Pt.Electrode

Hg   Hg

Membrane
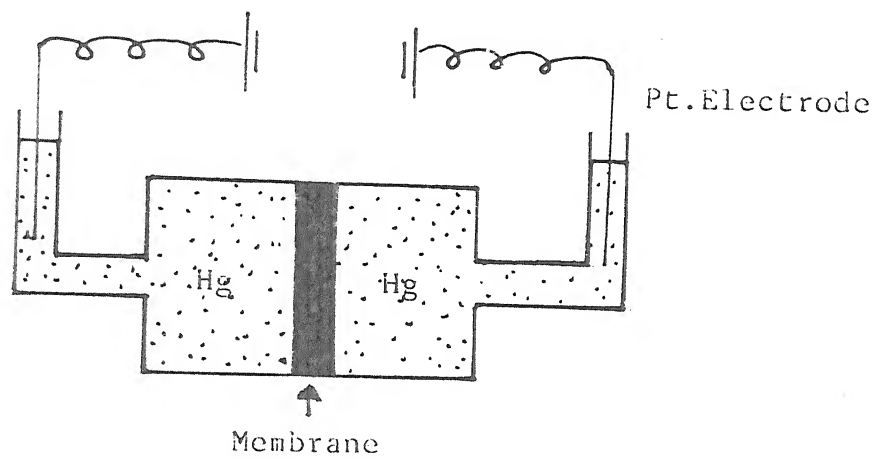
Fig.2.1 Cell for measuring the
electrical conductance.

total biionic potentia E for counterions of equal valance is given by

$$E = \frac{RT}{F} \ln \frac{\overline{D}_i a'_i \overline{\tau}_j}{\overline{D}_j a''_j \overline{\tau}_i} \qquad (2.1)$$

where a'_i/a''_j, $\overline{D}_i/\overline{D}_j$, $\overline{\tau}_i/\overline{\tau}_j$ are the activity ratios of the solutions, diffusion coefficient of ions in the membrane phase, and the ratio of the activity coefficients of ions. The symbols R,T,Z and F have their usual meanings. Equation (2.1) reduces to the form [eq. (2.2)] given by Wyllie and Kanaan (33,34):

$$E = \frac{RT}{F} \ln \frac{a_i \overline{U}_i}{a_j \overline{U}_j} \qquad (2.2)$$

provided $\overline{\tau}_i = \overline{\tau}_j$ and the diffusion coefficients are replaced by mobilities (33). Wyllie (34) expressed the intramembrane mobility ratio as

$$\frac{\overline{U}_i}{\overline{U}_j} = \frac{\overline{t}_i}{\overline{t}_i} = \frac{\overline{m}_i \overline{\lambda}_i}{\overline{m}_j \overline{\lambda}_j} \qquad (2.3)$$

where $\overline{t}_i/\overline{t}_j$ is the intramembrane transference ratio and $\overline{m}_i$ and $\overline{m}_j$ are the steady-state equilibrium concentration of i and j in the respective junction zone; $\overline{\lambda}_i$ is the conductivity of the membrane when it is wholly in i form and $\overline{\lambda}_j$ is the conductivity of the membrane when it is wholly in j form. furthermore, it was shown that $\overline{m}_i/\overline{m}_j \approx K_{ji}$, the selectivity. This, on substitution into eq. (2.3), gives

$$\frac{\overline{U}_i}{\overline{U}_j} = K_{ji} \left(\frac{\overline{\lambda}_i}{\overline{\lambda}_j}\right) \qquad (2.4)$$

Thus the ratio of mobilities were related to the chemical and electrical properties of the membrane.

Biionic potential measurements were also carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The values of biionic potential across parchment supported mercuric, nickel sulphide membranes and hen egg shell membrane with various 1:1 electrolyte combinations at different concentration are given in Tables 2.1-2.3 and plotted in Figs.(2.2-2.4). Equation (2.2) was used to calculated the intramembrane mobility ratio $\overline{U}_i/\overline{U}_j$. The values of $\overline{U}_i/\overline{U}_j$ thus calculated are given in Tables 2.4-2.6. An interesting point with regard to the value of $\overline{U}_i/\overline{U}_j$ is that the mobility ratio undergoes considerable change with the concentration of the external solutions and this behavior was seen with each electrolyte pair.

To gain knowledge of selectivity K_{ij} from the predetermined values of $\overline{U}_i/\overline{U}_j$ the ratio of electrical conductivities $\overline{\lambda}_i/\overline{\lambda}_j$, demanded by eq. (2.4), must be known. Membrane conductance measurements were carried out when it was wholly in form i or form j. The values of membrane conductance at various electrolyte concentrations are given in Tables 2.7-2.9. These values are relatively more dependent on the concentration of the electrolytes within the membrane as shown in Figs.(2.5-2.7), this implies that the membranes have a relatively high Donnan uptake of anion and a

TABLE 2.1

EXPERIMENTALLY OBSERVED VALUES OF BIIONIC POTENTIAL E (mV)
ACROSS MERCURIC SULPHIDE MEMBRANE AT 25 ± 0.1 $^{\circ}$C

Membrane	Mercuric sulphide		
Electrolyte pair	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration (M)			
0.1/0.1	6.5	1.1	6.8
0.05/0.05	7.2	1.5	7.5
0.02/0.02	8.4	2.8	10.1
0.01/0.01	10.4	6.5	12.1
0.005/0.005	11.5	7.2	17.7
0.002/0.002	12.0	7.5	18.2
0.001/0.001	12.2	8.0	18.9

vide Fig. 2.2

TABLE 2.2

EXPERIMENTALLY OBSERVED VALUES OF BIIONIC POTENTIAL E (mV) ACROSS NICKEL SULPHIDE MEMBRANE AT $25 \pm 0.1\ ^{\circ}C$

Membrane	Nickel sulphide		
Electrolyte pair	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration (M)			
0.1/0.1	3.0	5.8	5.0
0.05/0.05	3.6	6.1	5.4
0.02/0.02	4.8	7.4	6.4
0.01/0.01	5.7	9.3	8.1
0.005/0.005	6.9	10.6	9.7
0.002/0.002	8.1	12.7	11.3
0.001/0.001	8.3	13.0	11.5

Vide Fig. 2.3
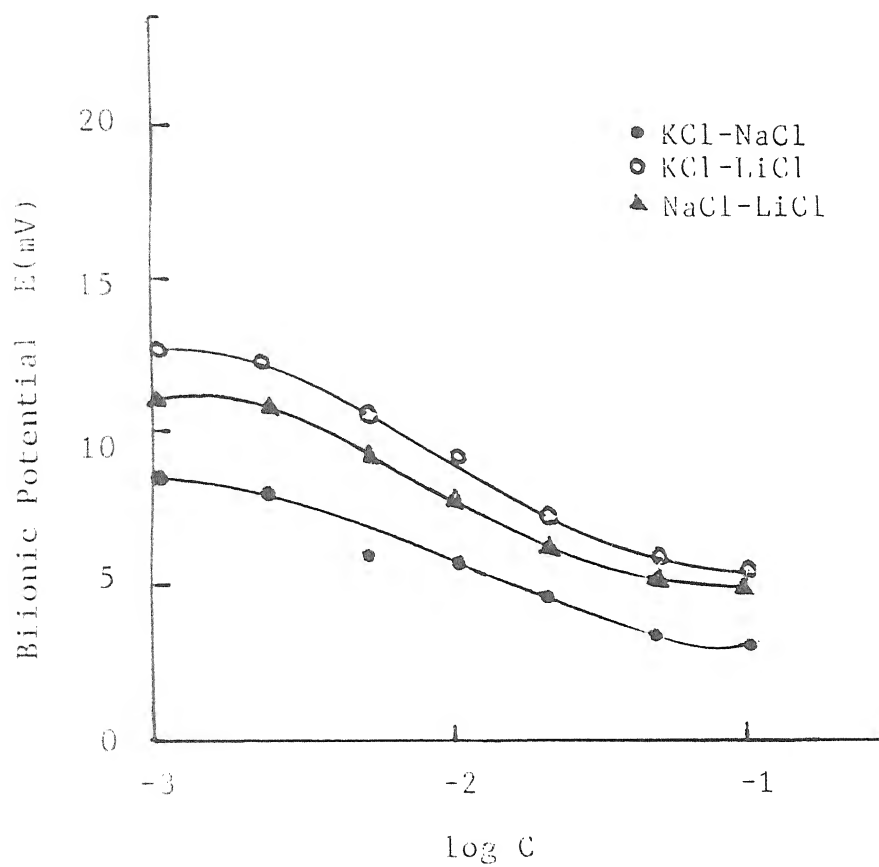
Fig.2.3. Plots of biionic potential E(mV) against
log C for nickel sulphide membrane using
1:1 electrolyte pairs.

TABLE 2.3

EXPERIMENTALLY OBSERVED VALUES OF BIIONIC POTENTIAL E (mV) ACROSS HEN EGG SHELL MEMBRANE AT $25\pm0.1\ ^{\circ}C$

Membrane	Hen egg shell		
Electrolyte pair	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration (M)			
0.1/0.1	1.4	-4.3	-4.2
0.05/0.05	1.9	-2.1	-1.8
0.02/0.02	2.6	-0.5	0.5
0.01/0.01	3.8	2.8	1.0
0.005/0.005	5.0	6.1	1.8
0.002/0.002	8.8	9.6	2.3
0.001/0.001	10.2	12.3	4.5

Vide Fig. 2.4
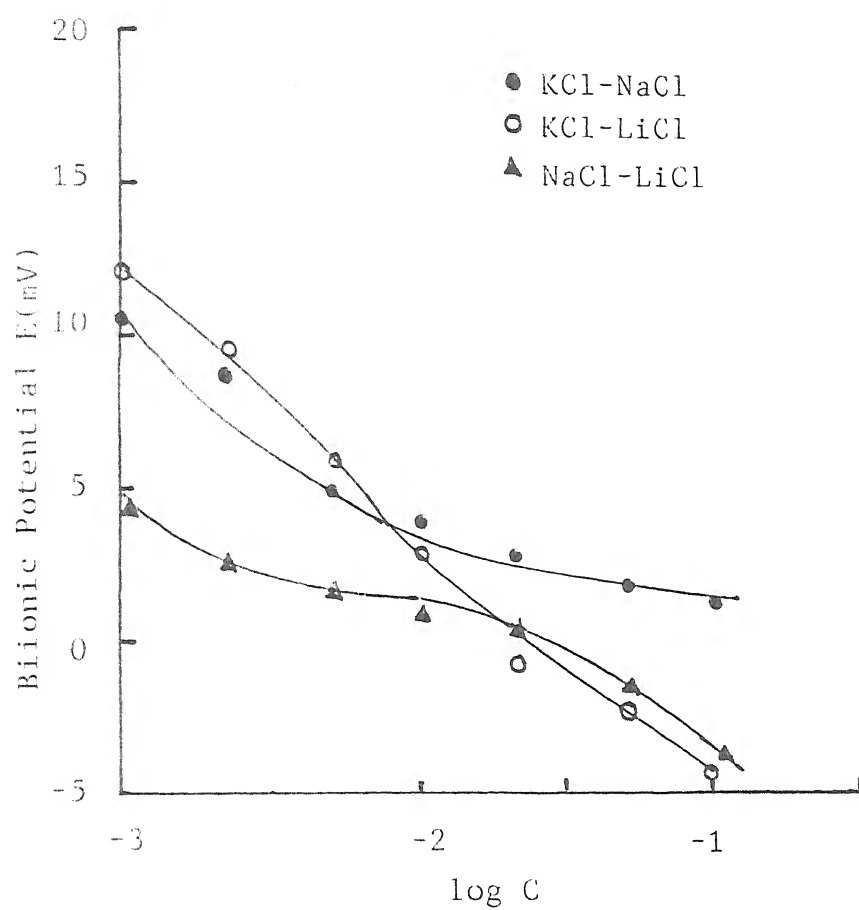
Fig.2.4.Plots of biionic potential E(mV)
against log C for hen egg shell
membrane using 1:1 electrolyte pairs.

TABLE 2.4

VALUES OF THE INTRAMEMBRANE MOBILITY RATIO OF VARIOUS 1:1 ELEC-
TROLYTE ION PAIRS ACROSS MERCURIC SULPHIDE MEMBRANE

Membrane	Mercuric sulphide		
Electrolyte ion pair	$\overline{U}_{K^+}/\overline{U}_{Na^+}$	$\overline{U}_{K^+}/\overline{U}_{Li^+}$	$\overline{U}_{Na^+}/\overline{U}_{Li^+}$
Concentration (M)			
0.1/0.1	1.01	1.32	1.17
0.05/0.05	1.04	1.34	1.22
0.02/0.02	1.10	1.53	1.42
0.01/0.01	1.21	1.74	1.75
0.005/0.005	1.27	1.99	1.83
0.002/0.002	1.38	2.21	1.94
0.001/0.001	1.52	2.39	1.97

TABLE 2.5

VALUES OF THE INTRAMEMBRANE MOBILITY RATIO OF VARIOUS 1:1 ELEC-
TROLYTE ION PAIRS ACROSS NICKEL SULPHIDE MEMBRANE

Membrane	Nickel sulphide		
Electrolyte ion pair	$\overline{U}_K^+ / \overline{U}_{Na}^+$	$\overline{U}_K^+ / \overline{U}_{Li}^+$	$\overline{U}_{Na}^+ / \overline{U}_{Li}^+$
Concentration (M)			
0.1/0.1	1.11	1.20	1.13
0.05/0.05	1.14	1.28	1.23
0.02/0.02	1.20	1.34	1.28
0.01/0.01	1.24	1.43	1.35
0.005/0.005	1.30	1.51	1.45
0.002/0.002	1.35	1.62	1.51
0.001/0.001	1.44	1.69	1.56

TABLE 2.6

VALUES OF THE INTRAMEMBRANE MOBILITY RATIO OF VARIOUS 1:1 ELEC-
TROLYTE ION PAIRS ACROSS HEN EGG SHELL MEMBRANE

Membrane	Hen egg shell		
Electrolyte ion pair	$\overline{U}_K^+ / \overline{U}_{Na}^+$	$\overline{U}_K^+ / \overline{U}_{Li}^+$	$\overline{U}_{Na}^+ / \overline{U}_{Li}^+$
Concentration (M)			
0.1/0.1	0.92	1.11	1.10
0.05/0.05	1.05	1.13	1.11
0.02/0.02	1.15	1.30	1.25
0.01/0.01	1.35	1.58	1.42
0.005/0.005	1.43	1.65	1.50
0.002/0.002	1.52	1.85	1.65
0.001/0.001	1.60	2.01	1.82

TABLE 2.7

EXPERIMENTALLY OBSERVED VALUES OF MEMBRANE ELECTRICAL CONDUCTANCE
(MHOS) ACROSS MERCURIC SULPHIDE MEMBRANE FOR MONOVALENT ELECTRO-
LYTES AT 25 ± 0.1 °C

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	0.85×10^{-1}	0.70×10^{-1}	0.65×10^{-1}
0.05/0.05	0.51×10^{-1}	0.44×10^{-1}	0.40×10^{-1}
0.02/0.02	2.57×10^{-2}	2.30×10^{-2}	2.20×10^{-2}
0.01/0.01	2.40×10^{-2}	2.20×10^{-2}	1.80×10^{-2}
0.005/0.005	1.90×10^{-2}	1.35×10^{-2}	1.20×10^{-2}
0.002/0.002	1.38×10^{-2}	1.25×10^{-2}	1.20×10^{-2}
0.001/0.001	0.92×10^{-2}	0.85×10^{-2}	0.63×10^{-2}

Vide Fig. 2.5

Fig.2.5. Plots of conductanceX10^2 (MHOS) Vs. -log C for mercuric sulphide membrane with 1:1 electrolytes.

TABLE 2.8

EXPERIMENTALLY OBSERVED VALUES OF MEMBRANE ELECTRICAL CONDUCTANCE (MHOS) ACROSS NICKEL SULPHIDE MEMBRANE FOR MONOVALENT ELECTRO-LYTES AT 25 ± 0.1 C

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	0.44×10^{-1}	0.38×10^{-1}	0.33×10^{-1}
0.05/0.05	0.40×10^{-1}	0.30×10^{-1}	0.25×10^{-1}
0.02/0.02	1.50×10^{-2}	1.30×10^{-2}	0.99×10^{-2}
0.01/0.01	1.15×10^{-2}	0.68×10^{-2}	0.65×10^{-2}
0.005/0.005	0.68×10^{-2}	0.48×10^{-2}	0.38×10^{-2}
0.002/0.002	0.50×10^{-2}	0.43×10^{-2}	0.40×10^{-2}
0.001/0.001	2.58×10^{-3}	2.50×10^{-3}	2.30×10^{-3}

Vide Fig. 2.6

TABLE 2.8

EXPERIMENTALLY OBSERVED VALUES OF MEMBRANE ELECTRICAL CONDUCTANCE (MHOS) ACROSS NICKEL SULPHIDE MEMBRANE FOR MONOVALENT ELECTROLYTES AT 25 ± 0.1 °C

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	0.44×10^{-1}	0.38×10^{-1}	0.33×10^{-1}
0.05/0.05	0.40×10^{-1}	0.30×10^{-1}	0.25×10^{-1}
0.02/0.02	1.50×10^{-2}	1.30×10^{-2}	$\cdot 0.99 \times 10^{-2}$
0.01/0.01	1.15×10^{-2}	0.68×10^{-2}	0.65×10^{-2}
0.005/0.005	0.68×10^{-2}	0.48×10^{-2}	0.38×10^{-2}
0.002/0.002	0.50×10^{-2}	0.43×10^{-2}	0.40×10^{-2}
0.001/0.001	2.58×10^{-3}	2.50×10^{-3}	2.30×10^{-3}

Vide Fig. 2.6
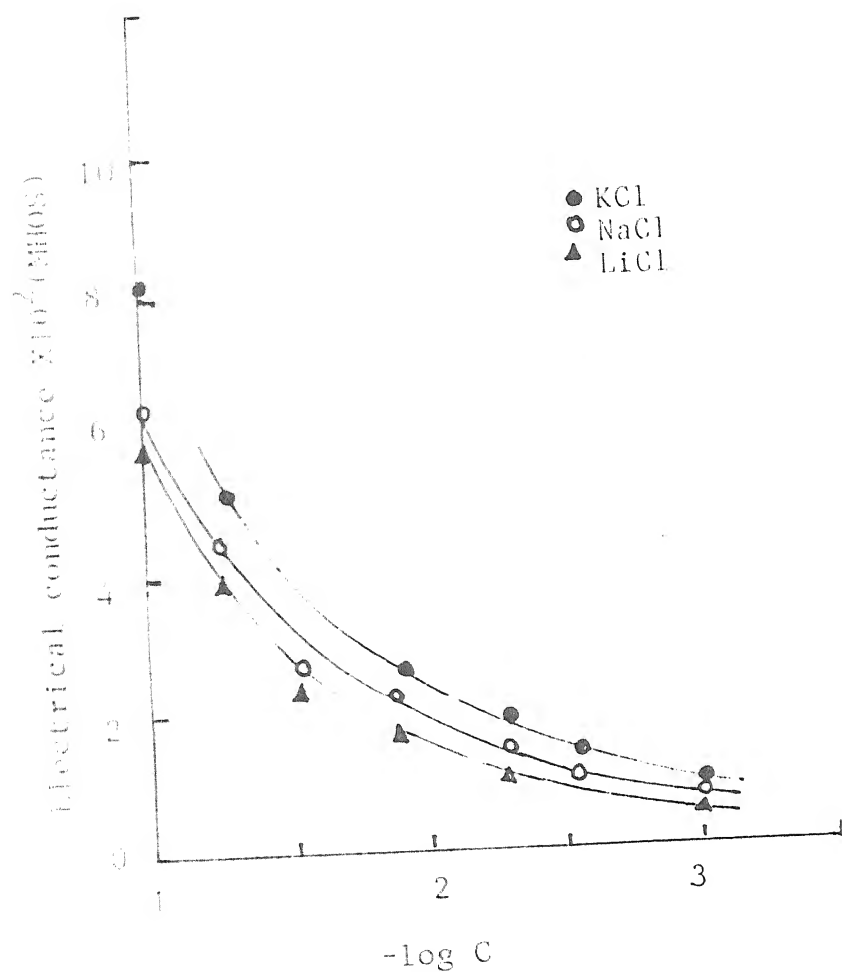
Fig.2.6. Plots of conductanceX10² (MHOS)
Vs.-log C for nickel sulphide
membrane with 1:1 electrolytes.

TABLE 2.9

EXPERIMENTALLY OBSERVED VALUES OF MEMBRANES ELECTRICAL CONDUCT-
ANCE (MHOS) ACROSS HEN EGG SHELL MEMBRANE FOR MONOVALENT ELECTRO-
LYTES AT $25 \pm 0.1^{\circ}$ C

Membrane	Hen egg shell		
Electrolyte	KCl	NaCl	LiCl
Concentrations (M)			
0.1/0.1	0.52×10^{-1}	0.47×10^{-1}	0.42×10^{-1}
0.05/0.05	0.45×10^{-1}	0.39×10^{-1}	0.34×10^{-1}
0.02/0.02	0.29×10^{-1}	0.26×10^{-1}	0.22×10^{-1}
0.01/0.01	0.22×10^{-1}	0.19×10^{-1}	0.17×10^{-1}
0.005/0.005	1.59×10^{-2}	1.50×10^{-2}	1.39×10^{-2}
0.002/0.002	2.40×10^{-3}	2.10×10^{-3}	1.30×10^{-3}
0.001/0.001	1.50×10^{-3}	1.10×10^{-3}	1.00×10^{-3}

Vide Fig. 2.7

.9
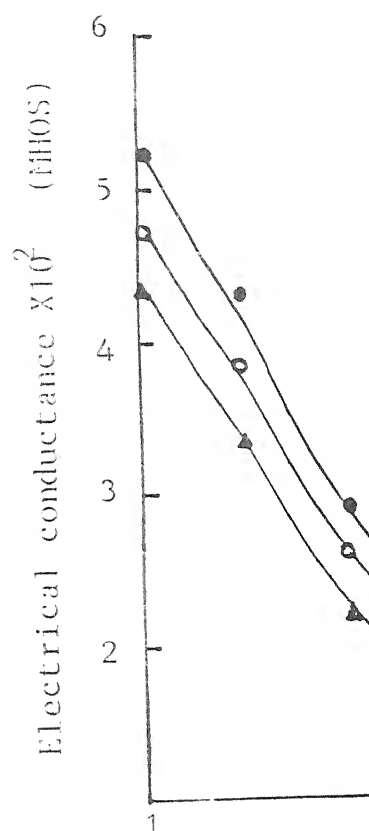
Fig.2.7. Plot
-log
with

egg shell

NaCl	LiCl
47×10^{-1}	0.42×10^{-1}
39×10^{-1}	0.34×10^{-1}
26×10^{-1}	0.22×10^{-1}
19×10^{-1}	0.17×10^{-1}
0×10^{-2}	1.39×10^{-2}
0×10^{-3}	1.30×10^{-3}
0×10^{-3}	1.00×10^{-3}

Electrical conductance $\times 10^2$ (MHOS)
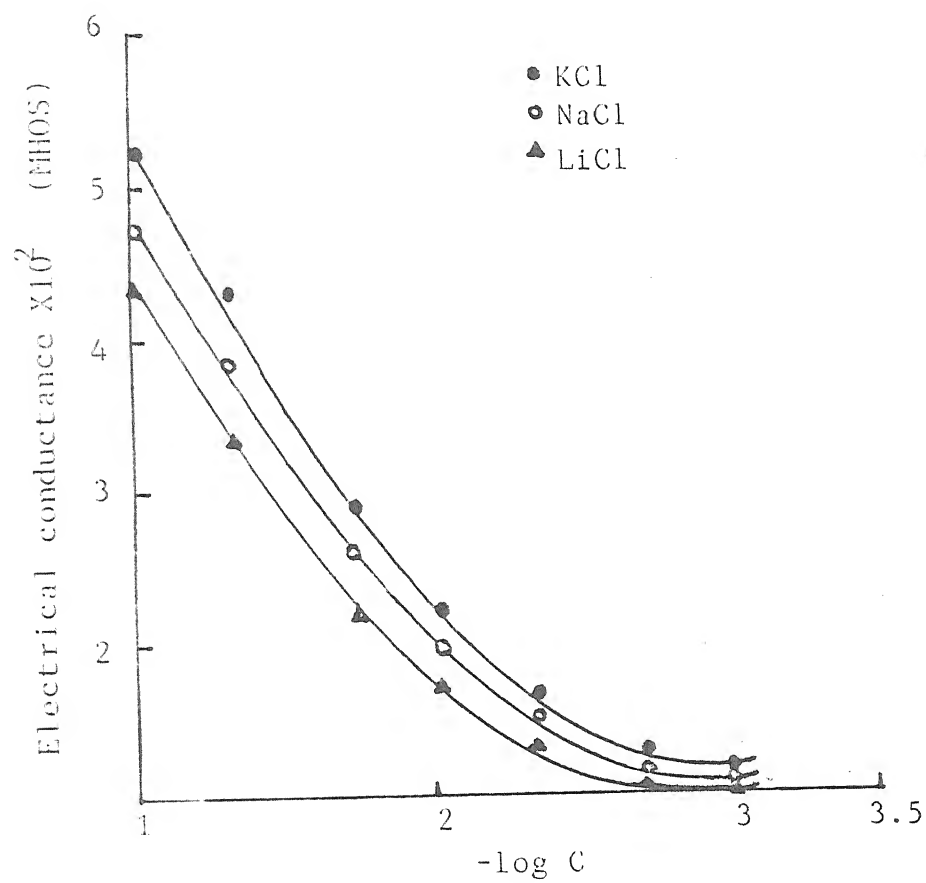
Fig.2.7. Plots of conductance$\times 10^2$(MHOS) Vs.
-log C for hen egg shell membrane
with 1:1 electrolytes.

low selectivity constant value. The values of selectivity K_{ij} evaluated from the mobilities ratio and the ratio of electrical conductivities using the data from Tables 2.4-2.6 and 2.7-2.9 are given in Tables 2.10-2.12. The intramembrane mobility ratio values also refer to the selectivity sequence of the membranes for the cations:

$$K^+ > Na^+ > Li^+$$

This order of selectivity on the basis of the Eisenman-Sherry model of membrane selectivity (35,36) points towards the weak field strength of the charge groups attached to the membrane matrix. This is an accordance with an earlier finding of charge density determinations of mercuric and nickel sulphide membranes and hen egg shell membrane, which have already been reported in previous chapter of membrne charge density.

In a number of theoritical papers (1,17,18,20,31,35, 37) different aspects of ion permeation in various membrane systems have been published. From thermodynamic treatment Sandblom and Eisenman (18) derived

$$\frac{P_i}{P_j} = K_{ji}\frac{\overline{U}_i}{\overline{U}_j} \qquad (2.5)$$

for fixed site membranes which implies that the permeability ratio is quite generally related to the ion exchange equilibrium constant K_{ij} and the ratio of mobilities of the critical ions, where K_{ij} is the ion exchange equilibrium constant defined by K_{ji}

TABLE 2.10

VALUES OF SELECTIVITY $K_{ji} \simeq (1/K_{ij})$ EVALUATED FROM INTRAMEMBRANE

MOBILITY RATIO AND THE RATIO OF ELECTRICAL CONDUCTIVITIES VARIOUS ELECTROLYTE CONCENTRATIONS FOR MERCURIC SULPHI MEMBRANE

Membrane	Mercuric sulphide		
Selectivity	K_{NaK}	K_{LiK}	K_{LiNa}
concentration (M)			
0.1/0.1	0.83	1.00	1.09
0.05/0.05	0.89	1.05	1.10
0.02/0.02	0.98	1.30	1.30
0.01/0.01	1.10	1.58	1.40
0.005/0.005	0.90	1.26	1.60
0.002/0.002	1.25	1.90	1.80
0.001/0.001	1.38	1.65	1.47

TABLE 2.11

VALUES OF SELECTIVITY $K_{ji} = (1/K_{ij})$ EVALUATED FROM INTRAMEMBRANE MOBILITY RATIO AND THE RATIO OF ELECTRICAL CONDUCTIVITIES AT VARIOUS CONCENTRATION FOR NICKEL SULPHIDE MEMBRANE

Membrane	Nickel sulphide		
Selectivity	K_{NaK}	K_{LiK}	K_{LiNa}
Concentration (M)			
0.1/0.1	0.97	0.92	1.06
0.05/0.05	0.87	0.90	1.18
0.02/0.02	1.04	0.89	0.71
0.01/0.01	1.15	0.81	0.93
0.005/0.005	0.93	0.91	1.25
0.002/0.002	1.16	0.92	0.95
0.001/0.001	1.33	1.42	1.42

TABLE 2.12

VALUES OF SELECTIVITY $K_{ji} \approx (1/K_{ij})$ EVALUATED FROM INTRAMEMBRANE MOBILITY RATIO AND THE RATIO OF ELECTRICAL CONDUCTIVITIES AT VARIOUS ELECTROLYTE CONCENTRATIONS FOR HEN EGG SHELL MEMBRANE

Membrane	Hen egg shell		
Selectivity	K_{NaK}	K_{LiK}	K_{LiNa}
Concentration (M)			
0.1/0.1	1.04	0.55	0.58
0.05/0.05	1.08	0.56	0.62
0.02/0.02	1.22	0.69	0.70
0.01/0.01	1.23	0.71	0.69
0.005/0.005	1.58	0.74	0.72
0.002/0.002	2.06	1.11	0.97
0.001/0.001	2.07	1.23	1.03

$= 1/K_{ij} = a_j c_i / a_i c_j$. Equation (2.5) suggests that the permeability ratio P_i/P_j can be calculated, provided that the mobility ratio $\overline{U}_i/\overline{U}_j$ and the ion exchange constant K_{ij} of a membrane for the ions are known. The values of permeability ratio devived in this way from the predetermined values of $\overline{U}_i/\overline{U}_j$ and K_{ij} for mercuric, nickel sulphide membranes and hen egg shell membrane are given in Tables 2.13-2.15. The data in Tables 2.13-2.15 show that the membranes are weakly selective and that the selectivity increases with a decrease in the concentration of the bathing solutions. This is in full agreement with our earlier findings of membrane potential measurements with inorganic precipitate membranes (3).

Biionic potential [32,38] is also defined again as the membrane potential across a membrane which separates two electrolyte solutions with different concentrations, i.e. different mobile ions carrying the charge opposite to the fixed charge on the membrane. The emf (biionic potential) of the membrane using the cell of the type shown in the experimental part of this chapter has been related to the fixed charge concentration ($\emptyset X$) by the equation :

$$E_{BIP} = \frac{RT}{F} \ln \frac{\sqrt{1+(\emptyset_X M_A/2a)^2} - (\emptyset_X M_A/2a)}{\sqrt{1+(\emptyset_X M_B/2a)^2} - (\emptyset_X M_B/2a)} \qquad (2.6)$$

where $\emptyset_X M_A$ and $\emptyset_X M_B$ are the concentrations of the fixed ions on the membrane phase. Equation (2.6) can be used to calculate

TABLE 2.13

VALUES OF PERMEABILITY RATIO (P_i/P_j) ACROSS MERCURIC SULPHIDE

MEMBRANE FOR MONOVALENT ELECTROLYTES AT VARIOUS CONCENTRATIONS

Membrane	Mercuric sulphide		
Permeability ratio	P_K^+ / P_{Na}^+	P_K^+ / P_{Li}^+	P_{Na}^+ / P_{Li}^+
Concentration (M)			
0.01/0.1	0.83	1.27	1.32
0.05/0.05	0.92	1.34	1.40
0.02/0.02	1.07	1.84	1.98
0.01/0.01	1.33	2.45	2.74
0.005/0.005	-	2.92	2.50
0.002/0.002	1.58	3.49	-
0.001/0.001	1.90	-	3.94

TABLE 2.14

VALUES OF PERMEABILITY RATIO (P_i/P_j) ACROSS NICKEL SULPHIDE

MEMBRANE FOR MONOVALENT ELECTROLYTES AT VARIOUS CONCENTRATIONS

Membrane	Nickel sulphide		
Permeability ratio	P_K^+ / P_{Na}^+	P_K^+ / P_{Li}^+	P_{Li}^+ / P_{Na}^+
Concentration (M)			
0.1/0.1	1.3	1.1	1.1
0.05/0.05	1.4	1.2	1.2
0.02/0.02	1.5	1.2	1.3
0.01/0.01	1.7	1.3	1.9
0.005/0.005	1.8	1.4	2.1
0.002/0.002	1.8	1.5	2.3
0.001/0.001	1.9	1.6	2.3

TABLE 2.15

VALUES OF PERMEABILITY RATIO (P_i/P_j) ACROSS HEN EGG SHELL MEM-
BRANE FOR MONOVALENT ELECTROLYTES AT VARIOUS CONCENTRATIONS

Membrane	Hen egg shell		
Permeabiliy ratio	P_K^+ / P_{Na}^+	P_K^+ / P_{Li}^+	P_{Li}^+ / P_{Na}^+
Concentration (M)			
0.1/0.1	1.0	0.7	0.7
0.05/0.05	1.1	0.8	0.8
0.02/0.02	1.2	0.95	1.0
0.01/0.01	1.2	1.0	1.0
0.005/0.005	1.6	1.1	1.1
0.002/0.002	2.0	1.5	1.3
0.001/0.001	2.1	1.8	1.4

biionic potential across a membrane provided effective fixed charge density of the membrane and the concentration of external electrolyte solutions are known. The values of biionic potential thus derived using predetermined values of effective fixed charge density of the membranes are given in Tables 2.16-2.18. For comparison the observed values are also given in the same tables. These values are closer to each other.

It is well known that biionic potential is a measure of selectivity (39) of membrane for ions of the same sign. Equation (2.7) has been found to predict similar to eq. (2.1) the values of biionic potential reasonably well, provided $\overline{\tau}_B/\overline{\tau}_A$ remains constant :

$$E = \frac{RT}{F} \ln \frac{\overline{U}_A a'_A \overline{\tau}_B}{\overline{U}_B a''_B \overline{\tau}_A} \qquad (2.7)$$

This equation can be written as

$$E = \frac{RT}{F} \ln \frac{\overline{U}_A a'_A}{\overline{U}_B a''_B} \quad (\text{if } \overline{\tau}_A = \overline{\tau}_B) \qquad (2.8)$$

and

$$E = \frac{RT}{F} \ln \frac{\overline{t}_A}{\overline{t}_B} \qquad (2.9)$$

where

$$\frac{\overline{t}_A}{\overline{t}_B} = \frac{\overline{U}_A a'_A \overline{\tau}_B}{\overline{U}_B a''_B \overline{\tau}_A}$$

provided that the Donnan ratio $\overline{a}_A/\overline{a}_B = \overline{a}'_A/\overline{a}''_B$ is established.

TABLE 2.16

BIIONIC POTENTIAL VALUES E (mV) (THEORITICAL AND EXPERIMENTAL-
                           BIP

LY OBSERVED) ACROSS MERCURIC SULPHIDE MEMBRANE

Membrane			Mercuric Sulphide			
Biionic potential	Experimental			Theoritical		
Electrolyte pair	KCl-NaCl	KCl-LiCl	NaCl-LiCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration (M)						
0.1/0.1	6.5	1.1	6.8	4.2	1.1	6.2
0.05/0.05	7.2	1.5	7.5	5.2	2.4	7.6
0.02/0.02	8.5	2.8	10.1	10.1	4.1	14.2
0.01/0.01	10.4	6.5	15.5	12.1	5.9	17.8
0.005/0.005	11.5	7.2	17.6	17.7	7.9	21.3
0.002/0.002	12.0	7.5	18.1	18.2	8.4	21.8
0.001/0.001	12.2	8.0	18.7	18.9	8.8	22.0

TABLE 2.17

BIIONIC POTENTIAL VALUES E$_{BIP}$ (mV) (THEORITICAL AND EXPERIMENTAL-

LY OBSERVED) ACROSS NICKEL SULPHIDE MEMBRANE

Membrane			Nickel Sulphide			
Biionic potential	Experimental			Theoritical		
Electro- lyte pair	KCl-NaCl	KCl-LiCl	NaCl-LiCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration (M)						
0.1/0.1	3.0	5.8	5.0	2.1	5.1	4.0
0.05/0.05	3.6	6.1	5.4	2.8	5.5	4.2
0.02/0.02	4.8	7.4	6.4	3.6	6.8	8.5
0.01/0.01	5.7	9.3	8.1	5.7	9.7	9.5
0.005/0.005	6.9	10.6	9.7	8.1	10.8	10.1
0.002/0.002	8.1	12.7	11.3	8.8	13.0	11.6
0.001/0.001	8.3	13.0	11.5	9.0	13.2	12.0

TABLE 2.18

BIIONIC POTENTIAL VALUES E$_{BIP}$ (mV) (THEORITICAL AND EXPERIMENTAL

LY OBSERVED) ACROSS HEN EGG SHELL MEMBRANE

Membrane	Hen egg shell					
Biionic potential	Experimental			Theoretical		
Electro-lyte pair	KCl-NaCl	KCl-LiCl	NaCl-LiCl	KCl-NaCl	KCl-LiCl	NaCl-LiCl
Concentration (M)						
0.1/0.1	1.4	-4.3	-4.2	1.6	-4.4	-4.1
0.05/0.05	1.9	-2.1	-1.8	2.0	-2.2	-1.8
0.02/0.02	2.6	-0.5	0.5	2.5	-0.5	-0.5
0.01/0.01	3.8	2.8	1.0	3.8	2.7	1.1
0.005/0.005	5.0	6.1	1.8	5.1	6.0	1.7
0.002/0.002	8.8	9.6	2.3	8.9	9.7	2.3
0.001/0.001	10.2	12.3	4.5	9.2	10.1	2.8

The biionic potential generated across nickel and mercuric sulphide membranes and hen egg shell membrane were measured keeping the concentration of AX constant and by varying concentration of BX, and again by keeping BX constant and varying AX. These measurements were extended to three solution pairs, i.e. KCL-NaCl, KCl-LiCl and NaCl-LiCl. The biionic potentials thus measured are given in Tables 2.19-2.21, these values are also shown in Figs. (2.8-2.10) as a function of $\log a_{AX}/a_{BX}$. Good straight lines as demanded by eq. (2.8) are obtained. The potential of intersection of the two straight lines at the same activity, i.e. $a_{AX}/a_{BX}=1$, gives the value of transport ratio using eq. (2.9). The transport ratio thus obtained for different 1:1 electrolyte pairs for mercuric and nickel sulphide membranes and hen egg shell mambrane are given in Table 2.22.

These results also point towards the order of selectivity of cations transporting through the membranes is as follows.

$$K^+ > Na^+ > Li^+$$

TABLE 2.19

EXPERIMENTAL VALUES OF BIIONIC POTENTIAL ACROSS MERCURIC SULPHIDE MEMBRANE KEEPING THE CONCENTRATION OF ONE ELECTROLYTE CONSTANT AND VARYING THE CONCENTRATION OF OTHER ELECTROLYTE AND VICE-VERSA

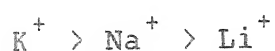| Membrane	Mercuric sulphide					
Electro-lyte pair	KCl-NaCl	NaCl-KCl	NaCl-LiCl	LiCl-NaCl	KCl-LiCl	LiCl-KCl
Concentration (M)						
0.1/0.05	15.4	1.5	10.3	-4.9	9.6	-4.2
0.1/0.01	19.1	-10.1	21.2	-20.1	18.2	-16.1
0.1/0.005	25.0	-18.8	31.4	-31.4	26.8	-24.3
0.1/0.001	30.2	-20.4	40.0	-42.5	35.7	-33.2

Vide Fig.2.8

TABLE 2.19

EXPERIMENTAL VALUES OF BIIONIC POTENTIAL ACROSS MERCURIC SULPHIDE
MEMBRANE KEEPING THE CONCENTRATION OF ONE ELECTROLYTE CONSTANT
AND VARYING THE CONCENTRATION OF OTHER ELECTROLYTE AND VICE-VERSA

Membrane	Mercuric sulphide					
Electro-lyte pair	KCl-NaCl	NaCl-KCl	NaCl-LiCl	LiCl-NaCl	KCl-LiCl	LiCl-KCl

Concentration
(M)

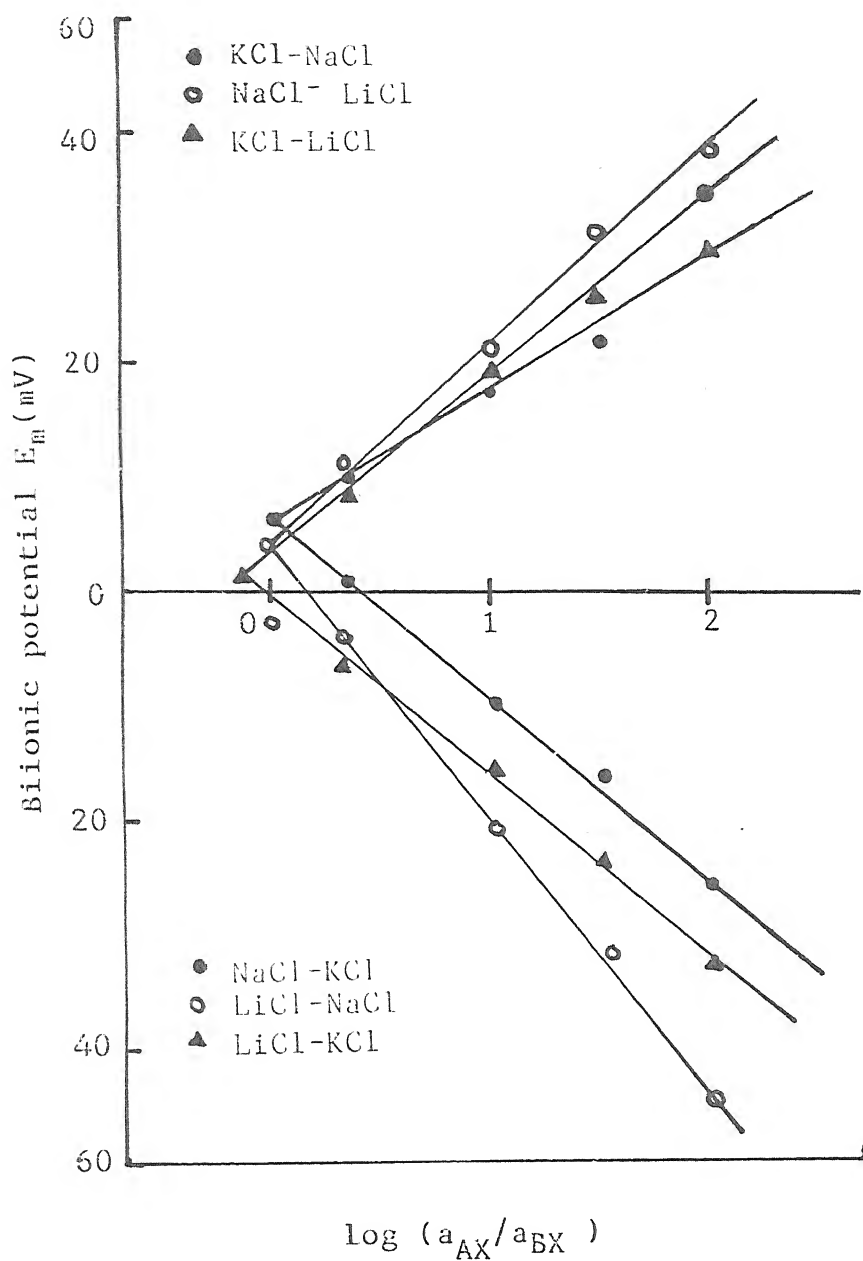|	KCl-NaCl	NaCl-KCl	NaCl-LiCl	LiCl-NaCl	KCl-LiCl	LiCl-KCl
0.1/0.05	15.4	1.5	10.3	-4.9	9.6	-4.2
0.1/0.01	19.1	-10.1	21.2	-20.1	18.2	-16.1
0.1/0.005	25.0	-18.8	31.4	-31.4	26.8	-24.3
0.1/0.001	30.2	-20.4	40.0	-42.5	35.7	-33.2

Vide Fig.2.8

Fig.2.8. Plots of biionic potential E_{BIP}(mV) against log (a_{AX}/a_{BX}) for mercuric sulphide membrane.

TABLE 2.20

EXPERIMENTAL VALUES OF BIIONIC POTENTIAL ACROSS NICKEL SULPHIDE
MEMBRANE KEEPING THE CONCENTRATION OF ONE ELECTROLYTE CONSTANT
AND VARYING THE CONCENTRATION OF OTHER AND VICE-VERSA

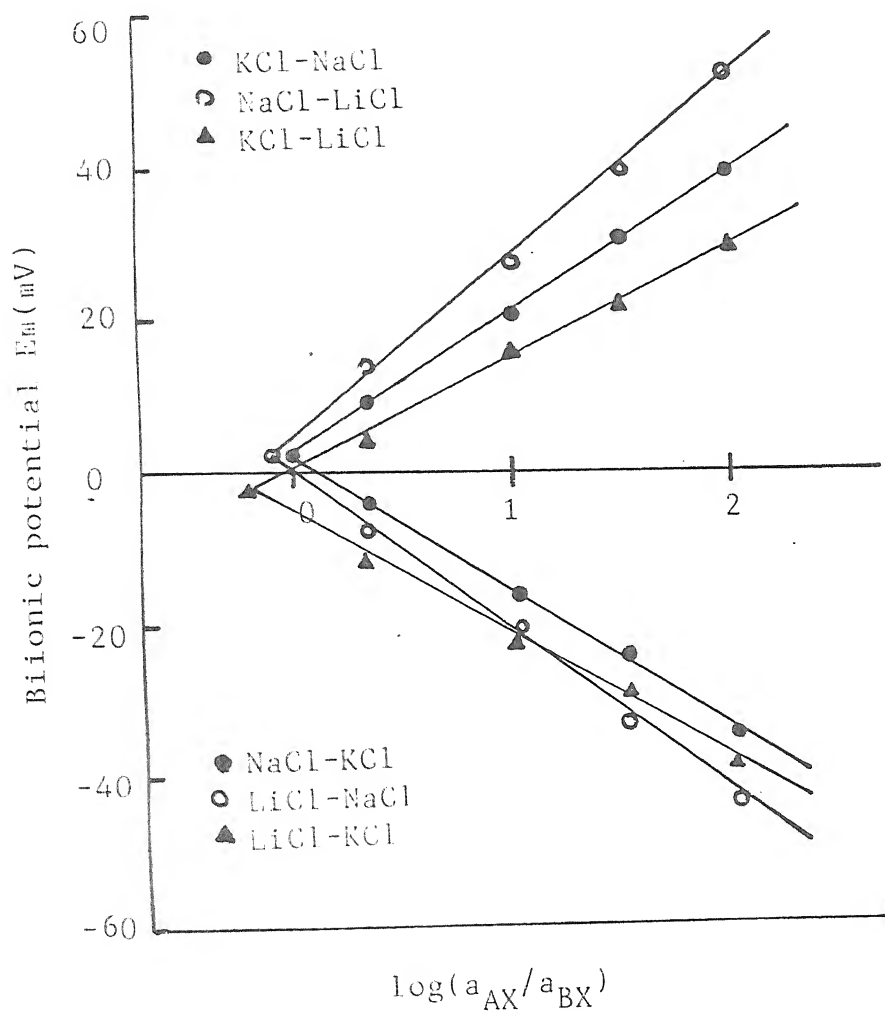| Membrane	Nickel sulphide					
Electro-lyte pair	KCl-NaCl	NaCl-KCl	NaCl-LiCl	LiCl-NaCl	KCl-LiCl	LiCl-KCl
Concentration (M)						
0.1/0.05	6.1	-4.1	14.4	-8.2	4.5	-11.8
0.1/0.01	20.2	-16.3	27.2	-20.1	15.3	-22.3
0.1/0.005	31.5	-25.0	40.1	-33.3	21.2	-30.1
0.1/0.001	35.2	-35.2	52.5	-43.3	30.3	-34.5

Vide Fig.2.9

Fig.2.9. Plots of biionic potential E_{BIP}(mV) against $\log(a_{AX}/a_{BX})$ for nickel sulphide membrane.

TABLE 2.21

EXPERIMENTAL VALUES OF BIIONIC POTENTIAL ACROSS HEN EGG SHELL
MEMBRANE KEEPING THE CONCENTRATION OF ONE ELECTROLYTE CONSTANT
AND VARYING THE CONCENTRATION OF OTHER ELECTROLYTE AND VICE-VERSA

Membrane	Hen egg shell					
Electro-lyte pair	KCl-NaCl	NaCl-KCl	NaCl-LiCl	LiCl-NaCl	KCl-LiCl	LiCl-KCl
Concentration (M)						
0.1/0.05	4.3	-11.8	10.1	-13.7	7.1	-15.2
0.1/0.01	23.7	-24.7	28.9	-32.5	17.2	-27.8
0.1/0.005	36.2	-33.2	45.2	-45.3	28.3	-40.1
0.1/0.001	50.0	-45.1	60.0	-56.8	35.3	-50.3

Vide Fig.2.10
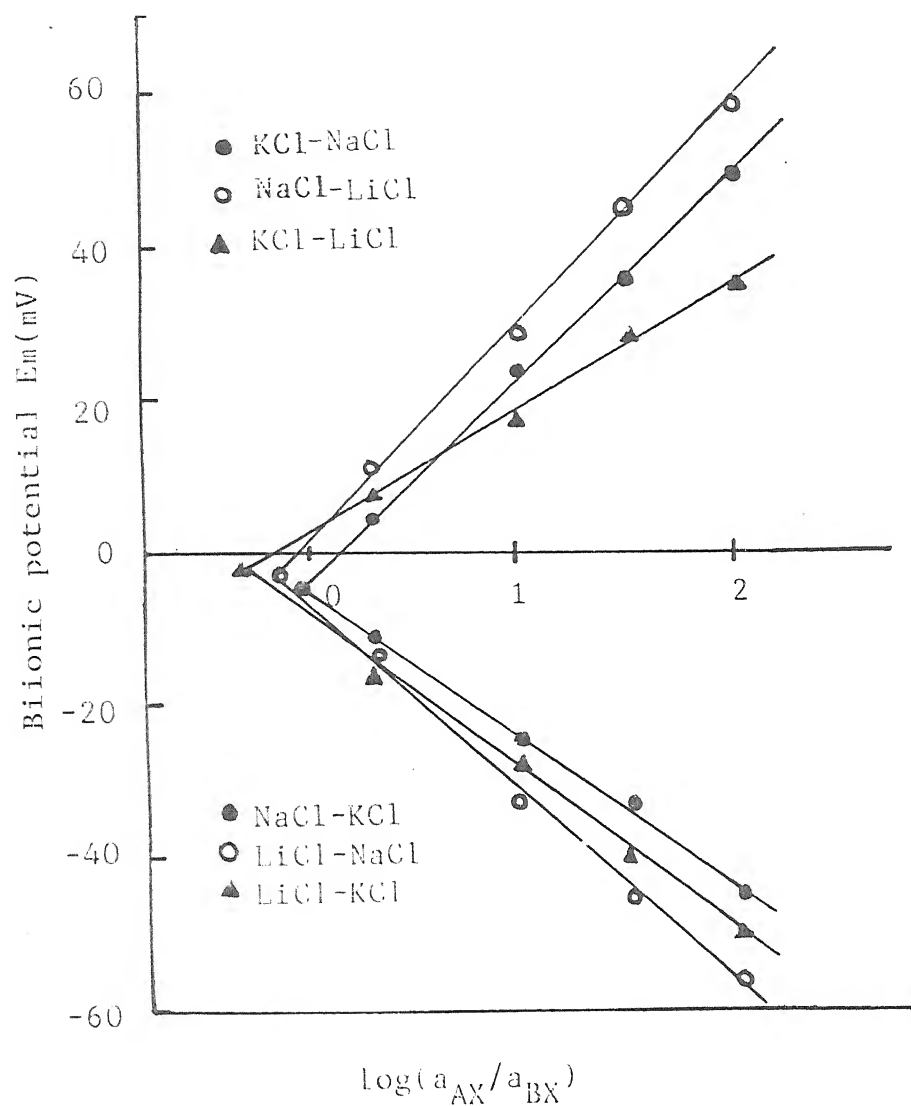
Fig.2.10. Plots of biionic potential E_{BIP}(mV) against $\log(a_{AX}/a_{BX})$ for hen egg shell membrane.

TABLE 2.22

VALUES OF TRANSPORT RATIO OBTAINED FOR DIFFERENT 1:1 ELECTROLYTE PAIRS ACROSS THE MERCURIC, NICKEL SULPHIDE MEMBRANES AND HEN EGG SHELL MEMBRANE

Membranes transport ratio	t_K^+ / t_{Na}^+	t_K^+ / t_{Li}^+	t_{Na}^+ / t_{Li}^+
Nickel sulphide	1.8	1.4	1.3
Mercuric sulphide	1.12	1.08	1.06
Hen egg shell	1.4	1.1	1.0

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CHAPTER - III

TRANSPORT MECHANISM OF SIMPLE METAL IONS THROUGH MEMBRANES

INTRODUCTION

Transport phenomena through membrnes in biological systems, as well as in many industrial processes, are important because of their potential use in various separation processes. Studies on the physicochemical aspects of membranes were started a few decades ago. An excellent monography by Lakshminarayanaiah covers progress in this field (1).

Extensive research work has been started to study the complex behaviour of biological membranes by developing various artificial membranes such as parchment supported or cellophane supported inorganic precipitates, which may mimic some properties of biological membranes in vivo (2-11). Moreover, transport of simple salts through polymers and polymeric network, charged or uncharged in closely related to ionic transport through the pores. Extensive work on the diffusion of simple salts in ion exchangers, either in the form of beads or membranes, and through weakly charged membranes, such as porous membranes containing inorganic precipitates, have been reported and reviewed comprehensively by Helfferich (12), Lakshminarayanaiah (1), Reichenberg (13) and Diamond and whitney (14).

Since membranes of biological origin are complex and not always easily reproducible, a number of researchers have used model systems for carrying out their studies of structure and dynamics of biomembrane systems (15-23). The findings of Teorell (24) that parchment supported membranes, in some formal aspects

at least behave exactly like gastric mucosal membranes, and those of Ayalon (25) that precipitation membranes may be useful as a model for the study of rectification phenomena in biological membranes, have encouraged the authors to investigate various aspect of membrane phenomena by taking the parchment supported precipitate membrane as a model system. On account of their stability and ion-exchanging power, such membranes may also find use in many processes like preparative organic electrochemistry, etc. (26,27).

Absolute reaction rate theory has been applied to diffusion processes in membrane by several investigators (28-33). Zwolinski, Eyring, and Reese (28) examined the available permeability data for various plant and animal cells by applying rate process theory. Similarly Schuler, Dames and Laidler (29) considered the Kinetics of membrane permeation of nonelectrolytes through colloidion membranes. Tien and Ting (7) studied water permeation through the lipid membranes and considered the permeation process from the stand point of rate process theory.Clough et al. (34), Li and Gainer (35), and Navari et al. (36) have applied absolute reaction rate theory to diffusion of solute in polymer solutions. They attached the importance to the influence of the polymer on diffusion activation energy. Kimikuza et al.(37) using an energy determine barrier theory have shown that diffusion coefficients of a calcium ion across the solution-membrane interface are proportional to the activity of the external calcium ion.Sa-

manta et al. (38) used the obsolute reaction rate theory to evaluate the energetics and the activation parameters for the movement of anions having potassium as comman cation partner in the microporous membranes. Recently, Tsimboukis and Petropoulos (39) determined the diffusion coefficient of alkali metal ions through cellulose membranes and discussed the results in terms of a pore structure model, and Iijima et al. (40) used activation analyses for investigating the mechanism of ion diffusion of simple salts through polyamide membranes.

Siddiqi et al. (15,41) evaluated the thermodynamic parameters of parchment supported membranes based on the application of irreversible thermodynamics and the theory of absolute reaction rate. Moreover, application of absolute reaction rate theory has also been use by Shyam et al. (42) in their ealier findings of transport through inorganic precipitate membranes.

However, in some more earlier communications it has been demonstrated that both parchment supported and polystyrene inorganic precipitate membranes possess a small quantity of fixed charges (43-47). To do this the author used the basis of Eisenman (48-50) and Sherry (51) model of membrane selectivity and, using membrane potential measurements, utilised various recently developed theories based on the principles of irreversible thermodynamics.

In this chapter conductivity at different temperatures of parchment supported mercuric and nickel sulphide membranes

bathed in different concentrations of alkali metal chlorides has been reported.Absolute reaction rate theory has also been applied in order to investigate the transport mechanism of simple metal ions through inorganic precipitate membranes.

EXPERIMENTAL

The parchment supported mercuric and nickel sulphide membranes were prepared by the method of interaction suggested by Shyam and co-workers (9-11,42,45-47) as described in previous chapters. The resulting membranes were washed thoroughly with deionized water to remove contamination and absorved chemicals on the membrane skeleton. The membranes then cut out into cercular disc form and sealed by an adhesive between two half cells of U type forming the electrochemical cell of the type shown in Fig.(3.1). The half cells were first filled with electrolyte solutions to equilibrate the membrane. The solutions were then replaced by purified mercury without removing the adhering sur- face liquid (52). Platinum electrodes dipping into mercury were used to establish electrical contact. The membrane conductance was monitored on a Direct Reading Conductivity Meter 303 (Sys- tronics) at frequency of 10^3 cps. All measurements were carried out using water thermostat maintained at temperatures of 25,30,35,40,45 and $50^{\circ}C$ ($\pm0.1^{\circ}C$). The electrolyte solutions were prepared from analytical grade reagents and deionized water. Extensive use of the method has indicated that for reproducible results there should be no trapped air, particularly at the

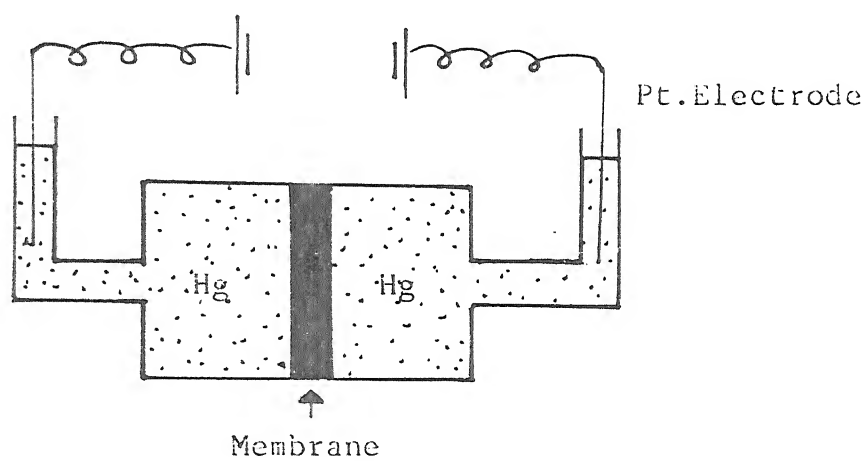Conductivity Bridge

Pt.Electrode

Membrane

Fig.3.1 Cell for measuring the
electrical conductance.

membrane mercury interface and that the mercury used should be purified as it is easily oxidized.

RESULTS AND DISCUSSION

The specific conductance values of the parchment supported mercuric and nickel sulphide membranes in contact with various 1:1 electrolyte solutions in a temperature range 25-50°C ($\pm$0.1°C) were measured which are given in Tables 3.1-3.12. These specific conductance values of the membranes are also shown in the Figs. (3.2-3.3). The specific conductance of the membranes first increases almost linearly with the square root of the concentration of the bathing electrolyte solutions and attains a maximum limiting value. This behaviour was seen with all the 1:1 electrolytes used at all temperatures. The flow of ions and water are generally larger in the more open structures of the membrane and decrease as the membrane shrinks in more concentrated solution. This is, in part at least, due to increased obstruction of the polymer matrix as diffusional pathways become more tortuous and fractional pore volume decreases. On the other hand electrical conductivity should increase with increased salt uptake. The observed values of electrical conductivity which bear the good agreement with the statement as given in the Tables 3.1-3.12 at respective temperatures. These two opposing effects operate simultaneously at higher concentrtions as shown in Figs.(3.4-3.9). The sequence of both the membranes conductance for alkali metal ions under the same conditions (0.01M,25°C) was

TABLE 3.1

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS MER

CURIC SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT

25±0.1 $^{\circ}$C

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	8.6×10^{-2}	7.0×10^{-2}	6.6×10^{-2}
0.05/0.05	5.6×10^{-2}	4.5×10^{-2}	4.0×10^{-2}
0.02/0.02	2.6×10^{-2}	2.3×10^{-2}	2.2×10^{-2}
0.01/0.01	2.4×10^{-2}	2.2×10^{-2}	1.8×10^{-2}
0.005/0.005	1.9×10^{-2}	1.4×10^{-2}	1.2×10^{-2}
0.002/0.002	1.4×10^{-2}	1.3×10^{-2}	1.2×10^{-2}
0.001/0.001	0.9×10^{-2}	0.9×10^{-2}	0.6×10^{-2}

TABLE 3.2

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS MER

CURIC SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTE AT

30 ± 0.1 $^{\circ}$C

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/1.0	9.6×10^{-2}	7.2×10^{-2}	6.6×10^{-2}
0.05/0.05	7.9×10^{-2}	6.2×10^{-2}	5.6×10^{-2}
0.02/0.02	5.8×10^{-2}	4.8×10^{-2}	3.8×10^{-2}
0.01/0.01	3.8×10^{-2}	3.0×10^{-2}	2.8×10^{-2}
0.005/0.005	2.8×10^{-2}	2.6×10^{-2}	2.0×10^{-2}
0.002/0.002	1.8×10^{-2}	1.8×10^{-2}	1.5×10^{-2}
0.001/0.001	1.2×10^{-2}	1.0×10^{-2}	0.8×10^{-2}

TABLE 3.3

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS MER

CURIC SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT

35 ± 0.1 $^{\circ}$C

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	10.5×10^{-2}	8.0×10^{-2}	7.3×10^{-2}
0.05/0.05	8.0×10^{-2}	7.1×10^{-2}	6.4×10^{-2}
0.02/0.02	7.2×10^{-2}	5.4×10^{-2}	4.9×10^{-2}
0.01/0.01	4.8×10^{-2}	3.4×10^{-2}	3.2×10^{-2}
0.005/0.005	3.8×10^{-2}	2.8×10^{-2}	2.5×10^{-2}
0.002/0.002	2.6×10^{-2}	1.9×10^{-2}	1.7×10^{-2}
0.001/0.001	1.6×10^{-2}	1.2×10^{-2}	1.0×10^{-2}

TABLE 3.4

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS MER

CURIC SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT

$40\pm0.1^{\circ}$C

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	12.0×10^{-2}	9.4×10^{-2}	7.8×10^{-2}
0.05/0.05	10.6×10^{-2}	8.0×10^{-2}	7.0×10^{-2}
0.02/0.02	8.4×10^{-2}	6.2×10^{-2}	5.2×10^{-2}
0.01/0.01	5.6×10^{-2}	4.0×10^{-2}	3.6×10^{-2}
0.005/0.005	4.4×10^{-2}	3.0×10^{-2}	2.8×10^{-2}
0.002/0.002	2.8×10^{-2}	2.0×10^{-2}	2.0×10^{-2}
0.001/0.001	1.8×10^{-2}	1.3×10^{-2}	1.2×10^{-2}

TABLE 3.5

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS MER

CURIC SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT

45 ± 0.1 $^\circ$C

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	12.8×10^{-2}	10.4×10^{-2}	8.8×10^{-2}
0.05/0.05	11.8×10^{-2}	9.6×10^{-2}	8.2×10^{-2}
0.02/0.02	9.6×10^{-2}	7.0×10^{-2}	5.8×10^{-2}
0.01/0.01	6.4×10^{-2}	5.4×10^{-2}	4.0×10^{-2}
0.005/0.005	4.6×10^{-2}	4.0×10^{-2}	2.9×10^{-2}
0.002/0.002	3.4×10^{-2}	2.2×10^{-2}	2.2×10^{-2}
0.001/0.001	1.8×10^{-2}	1.2×10^{-2}	1.3×10^{-2}

TABLE 3.6

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS MER

CURIC SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT

50 ± 0.1 $^{\circ}$C

Membrane	Mercuric sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	14.0×10^{-2}	11.4×10^{-2}	9.9×10^{-2}
0.05/0.05	13.2×10^{-2}	10.4×10^{-2}	9.0×10^{-2}
0.02/0.02	10.8×10^{-2}	8.2×10^{-2}	6.5×10^{-2}
0.01/0.01	7.0×10^{-2}	5.4×10^{-2}	4.2×10^{-2}
0.005/0.005	5.2×10^{-2}	4.2×10^{-2}	3.4×10^{-2}
0.002/0.002	3.8×10^{-2}	2.6×10^{-2}	2.6×10^{-2}
0.001/0.001	2.2×10^{-2}	1.3×10^{-2}	1.6×10^{-2}

TABLE 3.7

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm. $^{-1}$) ACROSS NICKEL SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT $25 \pm 0.1\ ^{\circ}C$

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	4.5×10^{-2}	3.8×10^{-2}	3.4×10^{-2}
0.05/0.05	4.0×10^{-2}	3.0×10^{-2}	2.8×10^{-2}
0.02/0.02	1.5×10^{-2}	1.3×10^{-2}	1.5×10^{-2}
0.01/0.01	1.2×10^{-2}	1.1×10^{-2}	0.7×10^{-2}
0.005/0.005	0.6×10^{-2}	0.5×10^{-2}	0.4×10^{-2}
0.002/0.002	0.5×10^{-2}	0.5×10^{-2}	0.3×10^{-2}
0.001/0.001	0.2×10^{-2}	0.2×10^{-2}	0.2×10^{-2}

TABLE 3.8

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS NICKEL SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT $30\pm0.1\,^{\circ}$C

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	5.3×10^{-2}	4.8×10^{-2}	4.0×10^{-2}
0.05/0.05	4.8×10^{-2}	4.4×10^{-2}	3.6×10^{-2}
0.02/0.02	3.8×10^{-2}	3.2×10^{-2}	2.6×10^{-2}
0.01/0.01	2.2×10^{-2}	2.0×10^{-2}	1.6×10^{-2}
0.005/0.005	1.8×10^{-2}	1.8×10^{-2}	1.2×10^{-2}
0.002/0.002	1.0×10^{-2}	1.0×10^{-2}	0.6×10^{-2}
0.001/0.001	0.6×10^{-2}	0.7×10^{-2}	0.4×10^{-2}

TABLE 3.9

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS NICKEL SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT $35 \pm 0.1\ ^{\circ}C$

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	6.6×10^{-2}	5.8×10^{-2}	4.8×10^{-2}
0.05/0.05	5.8×10^{-2}	5.4×10^{-2}	4.4×10^{-2}
0.02/0.02	4.4×10^{-2}	4.2×10^{-2}	3.6×10^{-2}
0.01/0.01	3.0×10^{-2}	2.8×10^{-2}	2.2×10^{-2}
0.005/0.005	2.2×10^{-2}	2.1×10^{-2}	1.6×10^{-2}
0.002/0.002	1.3×10^{-2}	1.3×10^{-2}	0.9×10^{-2}
0.001/0.001	0.8×10^{-2}	0.9×10^{-2}	0.6×10^{-2}

TABLE 3.10

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS NICKEL SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTE AT 40 ± 0.1 $^{\circ}$C

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	8.1×10^{-2}	6.6×10^{-2}	5.8×10^{-2}
0.05/0.05	7.0×10^{-2}	6.2×10^{-2}	5.4×10^{-2}
0.02/0.02	5.2×10^{-2}	4.8×10^{-2}	4.4×10^{-2}
0.01/0.01	3.2×10^{-2}	3.4×10^{-2}	2.8×10^{-2}
0.005/0.005	2.5×10^{-2}	2.6×10^{-2}	1.9×10^{-2}
0.002/0.002	1.4×10^{-2}	1.6×10^{-2}	1.1×10^{-2}
0.001/0.001	0.9×10^{-2}	1.0×10^{-2}	0.8×10^{-2}

TABLE 3.11

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS NICKEL SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT 45 ± 0.1 $^{\circ}$C

Membrane	Nickle sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	9.1×10^{-2}	7.8×10^{-2}	6.8×10^{-2}
0.05/0.05	8.0×10^{-2}	7.3×10^{-2}	6.4×10^{-2}
0.02/0.02	6.2×10^{-2}	5.6×10^{-2}	5.3×10^{-2}
0.01/0.01	3.8×10^{-2}	3.8×10^{-2}	3.4×10^{-2}
0.005/0.005	2.8×10^{-2}	3.0×10^{-2}	2.3×10^{-2}
0.002/0.002	1.6×10^{-2}	1.8×10^{-2}	1.4×10^{-2}
0.001/0.001	1.0×10^{-2}	1.2×10^{-2}	1.0×10^{-2}

TABLE 3.12

OBSERVED VALUES OF SPECIFIC CONDUCTANCE (MHOS Cm.$^{-1}$) ACROSS NICKEL SULPHIDE MEMBRANE FOR VARIOUS MONOVALENT ELECTROLYTES AT 50 ± 0.1 $^{\circ}$C

Membrane	Nickel sulphide		
Electrolyte	KCl	NaCl	LiCl
Concentration (M)			
0.1/0.1	9.8×10^{-2}	9.0×10^{-2}	8.0×10^{-2}
0.05/0.05	9.0×10^{-2}	8.4×10^{-2}	7.3×10^{-2}
0.02/0.02	7.2×10^{-2}	6.6×10^{-2}	6.2×10^{-2}
0.01/0.01	4.7×10^{-2}	4.4×10^{-2}	4.3×10^{-2}
0.005/0.005	3.4×10^{-2}	3.4×10^{-2}	3.0×10^{-2}
0.002/0.002	2.0×10^{-2}	2.2×10^{-2}	1.8×10^{-2}
0.001/0.001	1.2×10^{-2}	1.6×10^{-2}	1.2×10^{-2}
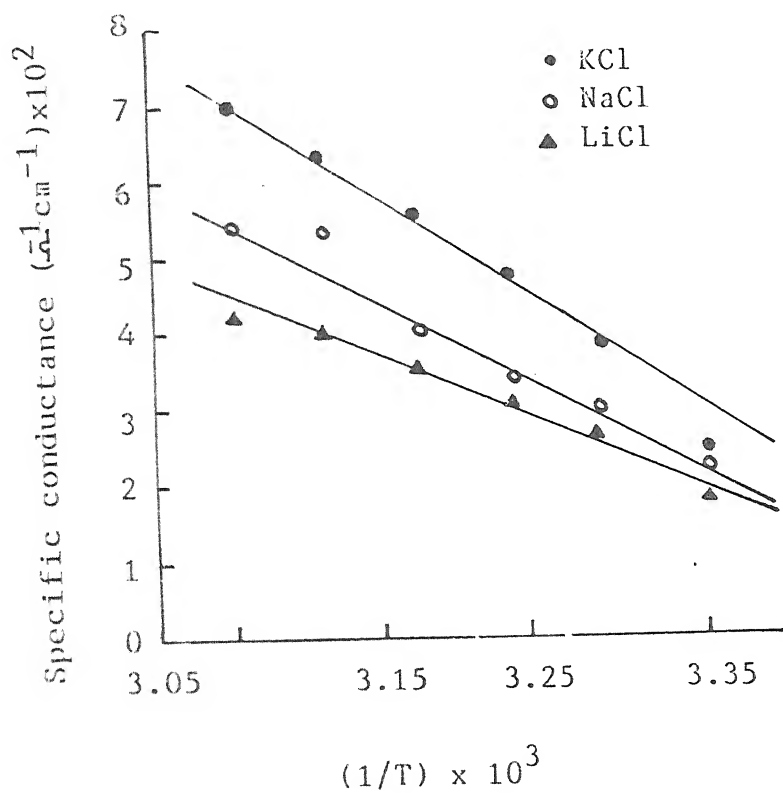
Fig.3.2. Arrhenius plot of specific conductance
values of mercuric sulphide membrane
for various 1:1 electrolytes.
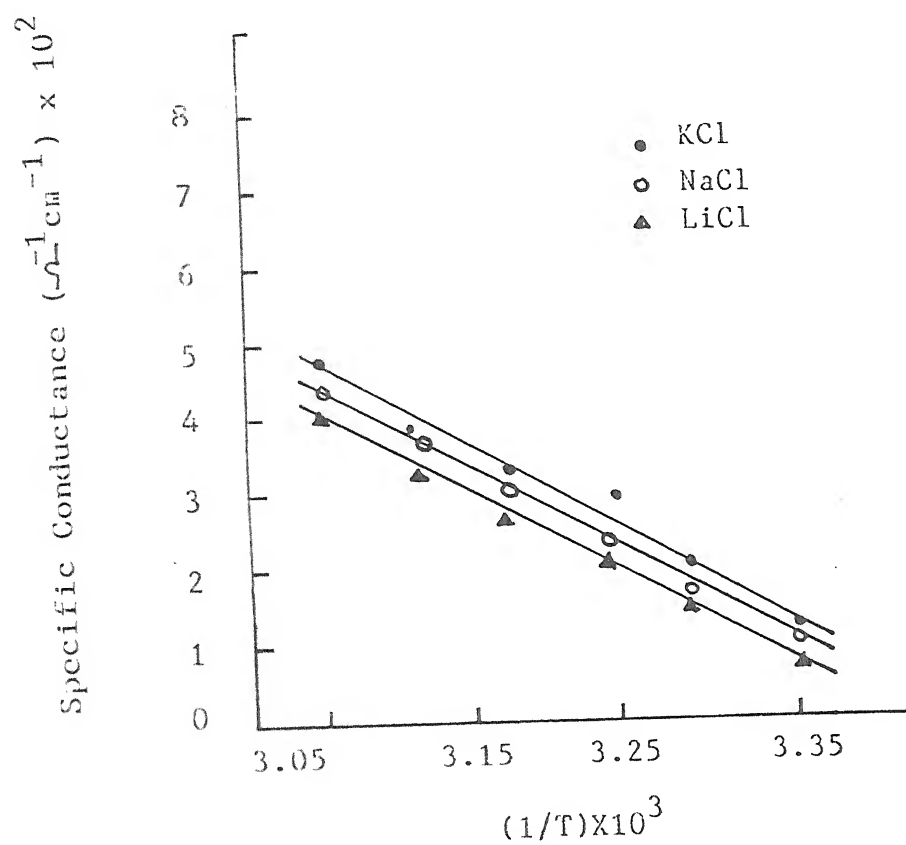
Fig. 3.3. Arrhenius plot of specific conductance values of nickel sulphide membrane for various 1:1 electrolytes.
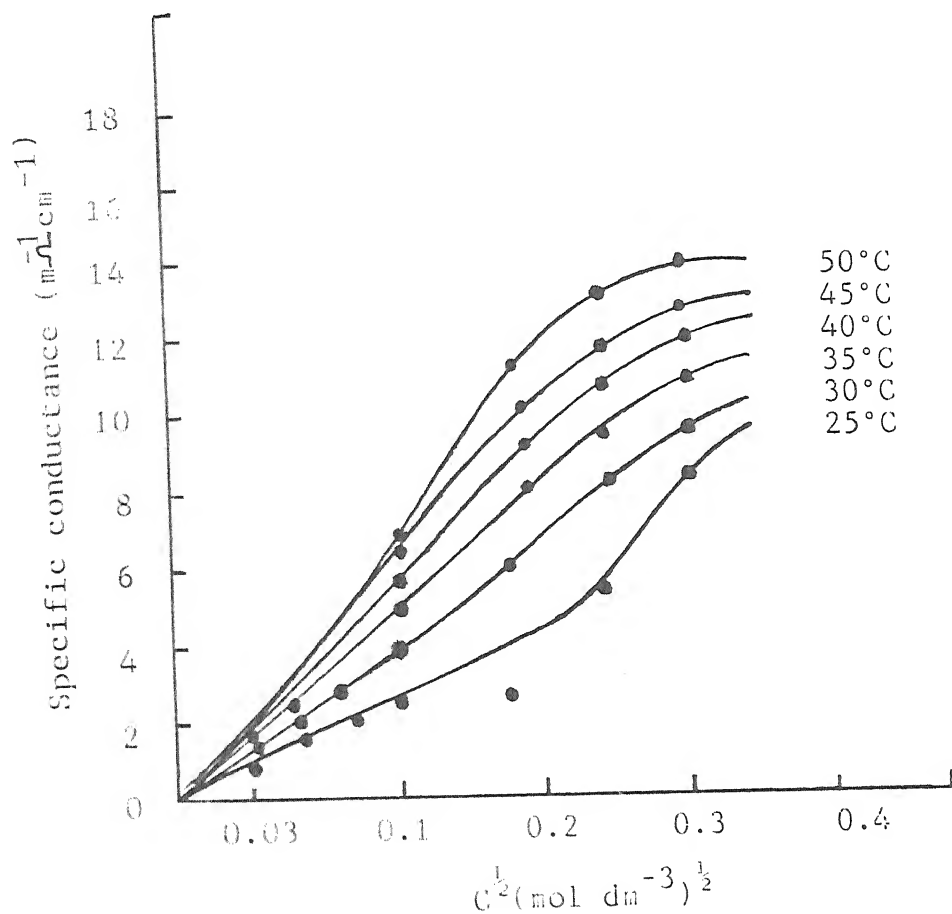
Fig.3.4. Plots of specific conductance $(m \Omega^{-1} cm^{-1})$ against square root of concentrations $(mol \ dm^{-3})^{\frac{1}{2}}$ for KCl at different temperatures through mercuric sulphide membrane.
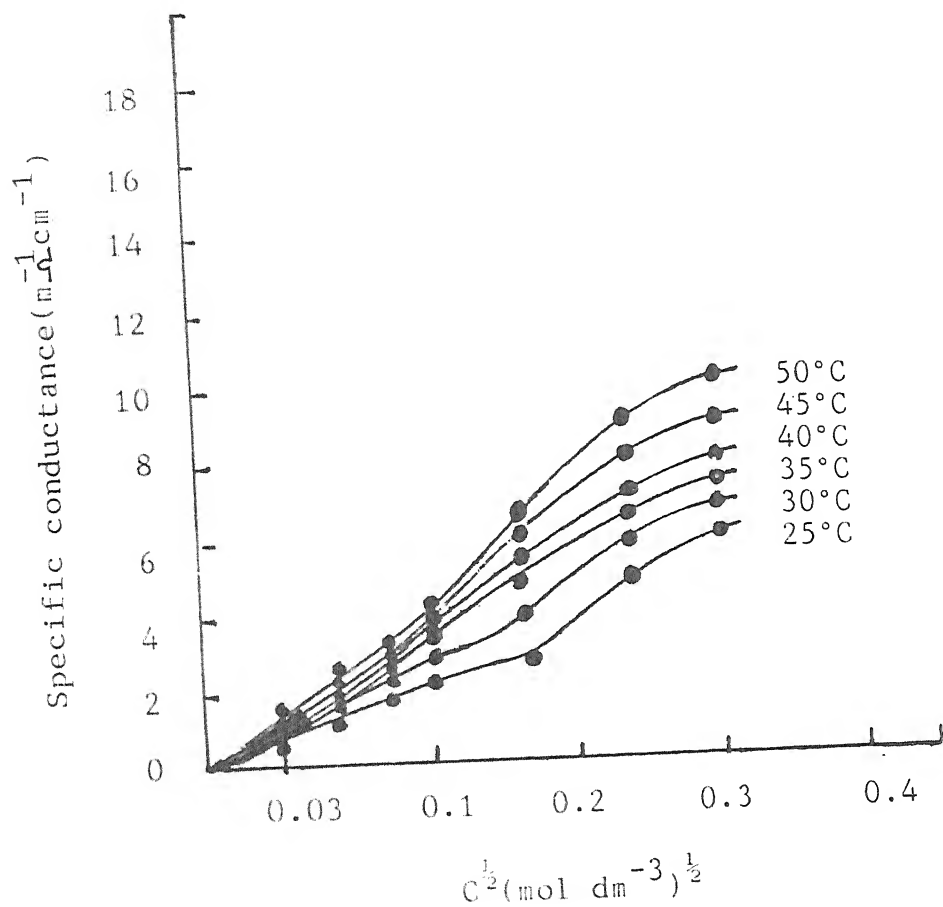
Fig.3.6. Plots of specific conductance $(m\,\Omega^{-1}cm^{-1})$ against square root of concentrations $(mol\ dm^{-3})^{\frac{1}{2}}$ for LiCl at different temperatures through mercuric sulphide membrane.
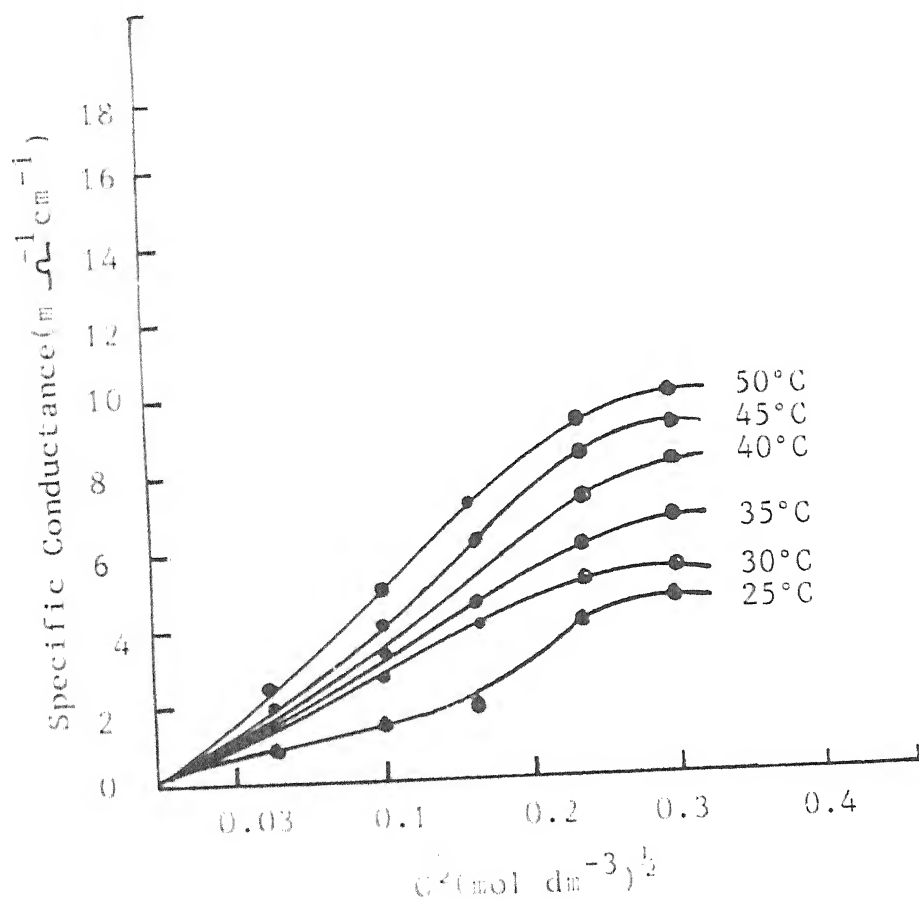
Fig.3.7. Plots of specific conductance(m Ω^{-1}cm^{-1}) against square root of concentrations (mol dm^{-3})$^{\frac{1}{2}}$ for KCl at different temperatures through nickel sulphide membrane.
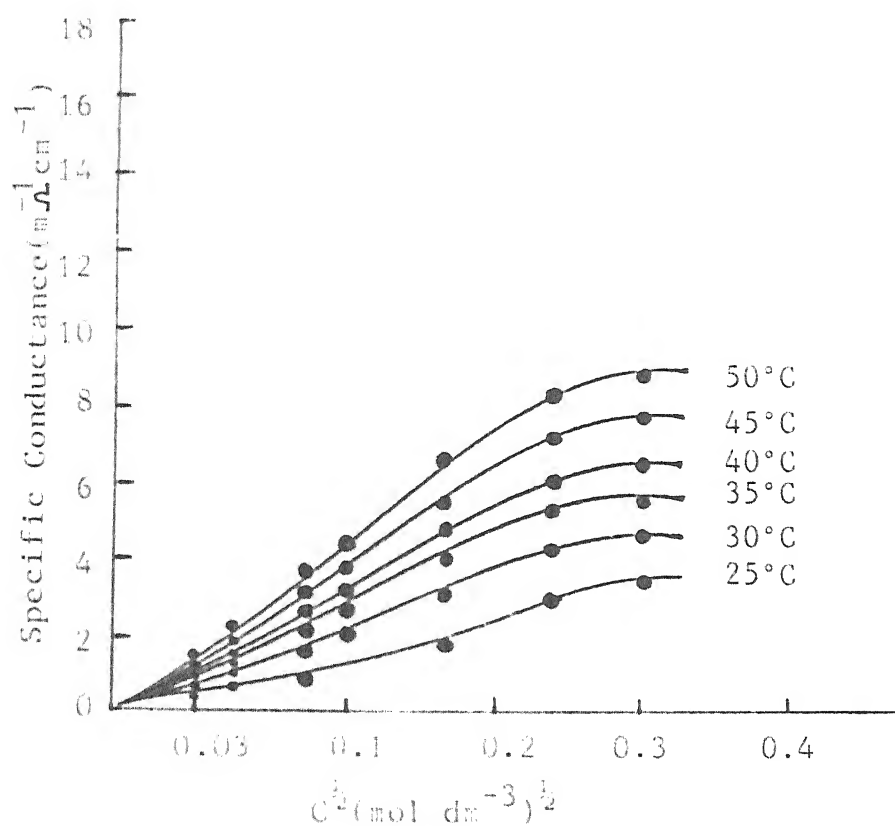
Fig.3.8. Plots of specific conductance($m \Omega^{-1} cm^{-1}$) against square root of concentrations $(mol \ dm^{-3})^{\frac{1}{2}}$ for NaCl at different temperatures through nickel sulphide membrane.
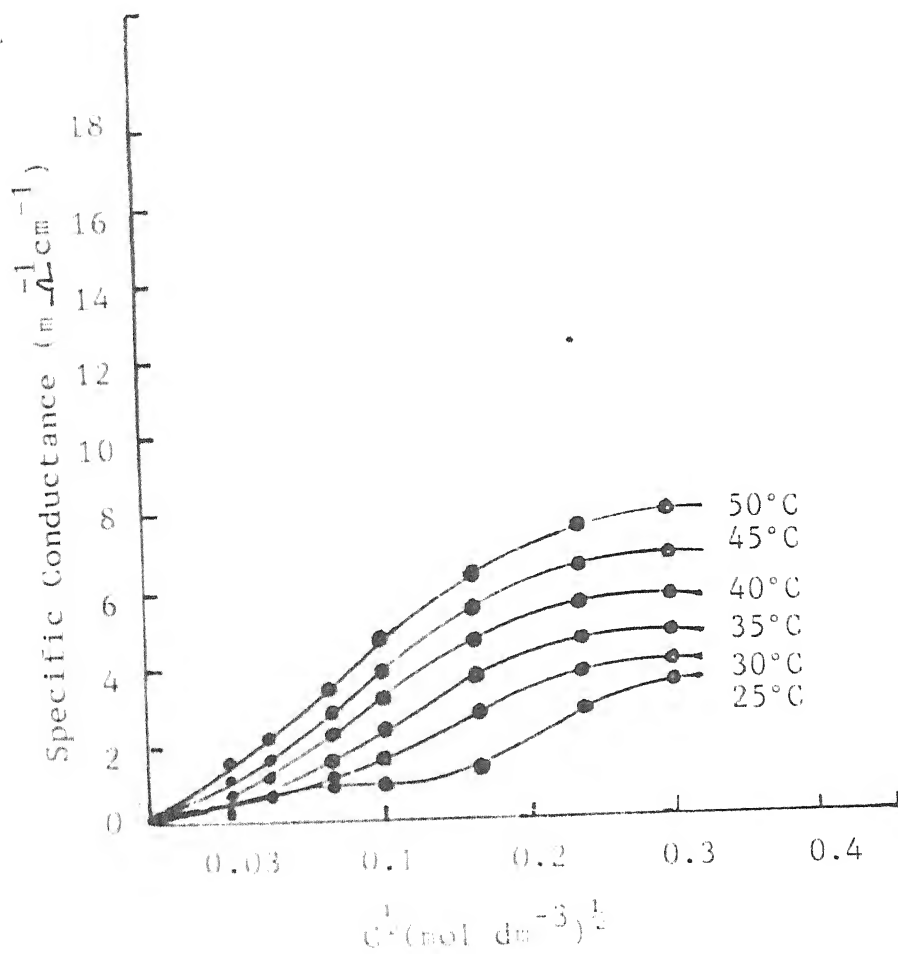
Fig. 3.9 . Plots of specific conductance (m Ω^{-1}cm^{-1}) against square root of concentrations (mol dm^{-3})$^{\frac{1}{2}}$ for LiCl at different temperatures through nickel sulphide membrane.

$$K^+ > Na^+ > Li^+$$
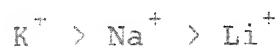
which is parallel to the mobility of alkali metal ions in aqueous solution. This sequence infers that the membranes are weakly charged (48-51) and that the ionic species at least partially retain their hydration shells (43). This is in full agreement with our results of charge density determinations(charge$\approx 10^{-3}$ meq/1). The selectivity of alkali metal ions in ion exchange resins have been discussed in detail by Reichenberg (53). The above sequence seems to be determined by membrane porosity in relation to size of the hydrated species flowing through it. Although the size of hydrated electrolytes is not known with certainty, there are a few tabulations (54-55) of the number of moles of water associated with some electrolytes.

In Figs.(3.10-3.11)plots of specific conductance of different electrolytes (chlorides) against free energy of hydration (ΔF^O) of cation (56) are given for the membranes. It is seen taht specific conductance values decrease with increasing hydration energy, that is greater size due to increasing hydration.This points to the facts that electrolyte is diffusing along pores or channels with dimensions adequate to allow the substance to penetrate the membranes. The state of hydration of the penetrating electolyte may be considered to exists in a dynamic condition so that, at higher temperatures, a considerably higher fraction of the total number of a given species would possess higher energy,ΔE per mole, this is according to the Boltzmann distribu-
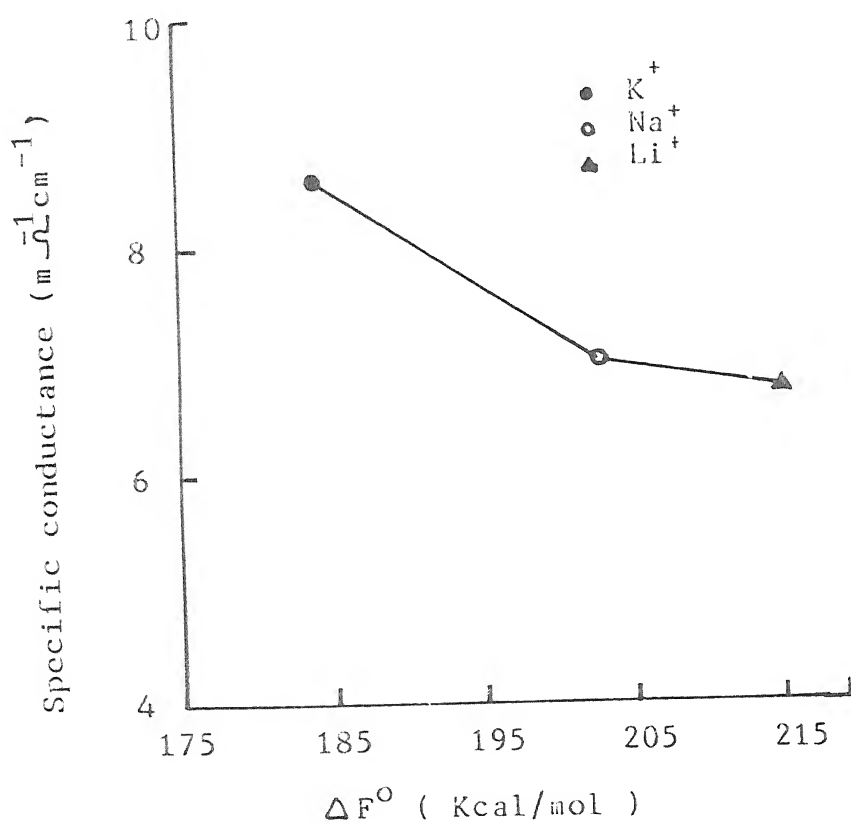
Fig. 3.10. Plots of specific conductance ($m \Omega^{-1} cm^{-1}$) of various 1:1 electrolytes at 25°C through mercuric sulphide membrane against free energy of hydration $\Delta F°$(Kcal/mol)of cations.
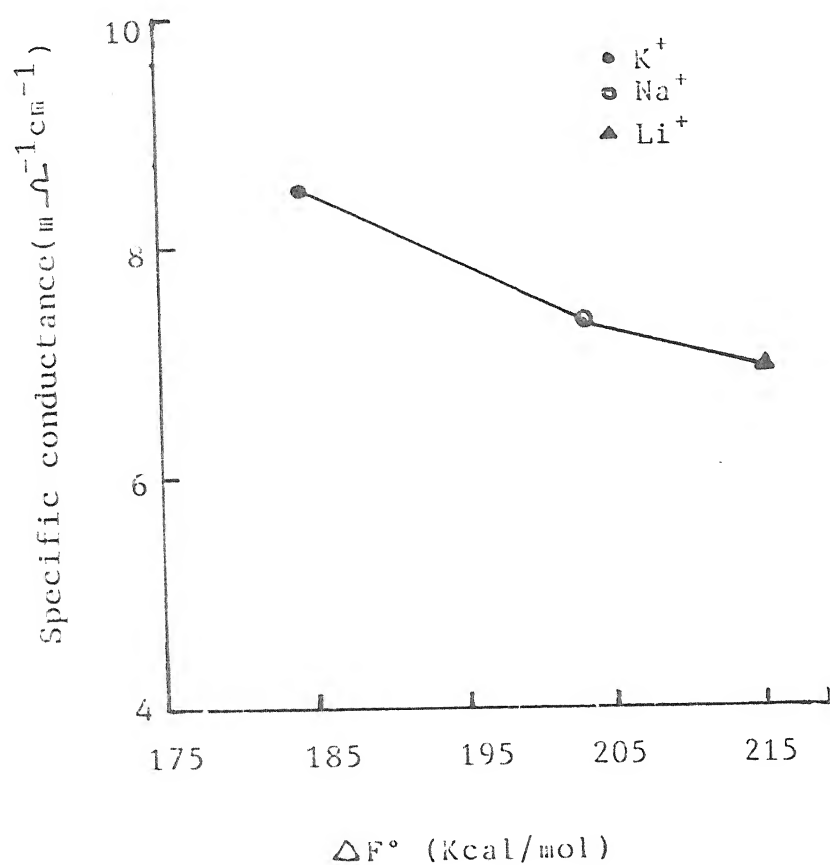
Fig.3.11. Plots of specific conductance ($m\ \Omega^{-1} cm^{-1}$) of various 1:1 electrolytes at 25°C through nickel sulphide membrane against free energy of hydration $\Delta F°$ (Kcal/mol) of cations.

tion $f=e^{-\Delta E/RT}$ (R is the gas constant). Under these circumstances, those ionic species which have lost sufficient water of hydration to be smaller than the size of the pore, would enter the membranes. In this way, the specific conductance would increase with increasing temperature, subject, however, to the proviso that the membranes have undergone no irreversible change in their structures. That no such structural change is involved is evident from the linear plots of obsorved specific conductence $(\Omega^{-1}cm^{-1})\times10^2$ Vs.$(1/T)\times10^3$ as shown in Figs.(3.2-3.3), the slope of which gives the activation energy as required by the Arrhenius equation. Tables 3.13 and 3.14 show that activation energy decreases with increasing concentration of the bathing electrolyte solution, and for different electrolytes at a particular concentration, it follows that:

$$E_{aK^+} > E_{aNa^+} > E_{aLi^+}$$

Activation energies for electrolytic conduction follow the sequence of crystallographic radii of the alkali metal cations, when penetrant moves in a polymeric substance containing relatively small amounts of water, its motion may be governed by the segmental mobility of the polymer and its diffusivity may depend on the probability that the segment will make a hole large enough to accommodate a penetrant species (57). In such a system the activation energy will depend on the size of the penetrant species; that is, the activation energy will increase with penetrant size. If this is the case in our system, the dependence of acti-

TABLE 3.13

CALCULATED VALUES OF THERMODYNAMIC PARAMETERS, ENERGY OF ACTIVA-
TION E_a, ENTHALPY OF ACTIVATION $\Delta H^{\neq}$, FREE ENERGY OF ACTIVATION
$\Delta F^{\neq}$ AND ENTROPY OF ACTIVATION $\Delta S^{\neq}$ FOR PARCHMENT SUPPORTED MERCURIC
SULPHIDE MEMBRANE IN CONTACT WITH DIFFERENT CONCENTRATION OF
VARIOUS 1:1 ELECTROLYTE SOLUTIONS

Membrane	Mercuric sulphide		
Electrolyte Concentration (mole dm^{-3})	Parameters		
	E_a (KCal mole^{-1})	$\Delta H^{\neq}$ (KCal mole^{-1})	$\Delta F^{\neq}$ (KCal mole^{-1})	$\Delta S^{\neq}$ (KCal mole^{-1} deg^{-1})
KCl				
0.1	3.01	2.30	17.21	52.20
0.01	5.02	3.02	18.75	53.85
0.001	8.50	3.25	19.10	54.15
NaCl				
0.1	2.12	1.85	17.70	54.21
0.01	3.80	2.10	18.30	54.28
0.001	5.98	2.25	18.58	54.62
LiCl				
0.1	1.25	0.75	17.12	53.80
0.01	1.51	1.05	17.80	54.82
0.001	1.80	2.10	18.10	55.46

TABLE 3.14

CALCULATED VALUES OF THERMODYNAMIC PARAMETERS, ENERGY OF ACTIVATION E_a , ENTHALPY OF ACTIVATION $\Delta H^{\neq}$, FREE ENERGY OF ACTIVATION $\Delta F^{\neq}$ AND ENTROPY OF ACTIVATION $\Delta S^{\neq}$ FOR PARCHMENT SUPPORTED NICKEL SULPHIDE MEMBRANE IN CONTACT WITH DIFFERENT CONCENTRATION OF VARIOUS 1:1 ELECTROLYTE SOLUTIONS

Membrane	Nickel sulphide			
Electrolyte Concentration (mole dm^{-3})	Parameters			
	E_a (KCal mole^{-1})	$\Delta H^{\neq}$ (KCal mole^{-1})	$\Delta F^{\neq}$ (KCal mole^{-1})	$\Delta S^{\neq}$ (KCal mole^{-1} deg^{-1})
KCl				
0.1	2.98	1.75	15.20	50.17
0.01	4.72	2.15	17.18	51.21
0.001	7.95	3.10	18.15	52.35
NaCl				
0.1	1.15	1.20	15.75	52.13
0.01	2.95	1.85	16.20	52.95
0.001	4.10	2.15	17.47	53.17
LiCl				
0.1	1.12	0.45	16.10	51.13
0.01	1.35	0.98	16.85	52.26
0.001	1.75	1.10	17.15	53.66

vation energy will increase with penetrant size. If this is the case in our system, the dependence of activation energy on the type of alkali metal ion may be interpreted in terms of the ion's crystallographic radius.

Using the work of Eyring (28,58), we have:

$$\Lambda = RT/Nh \ e^{-\Delta H^{\neq}/RT} \ e^{\Delta S^{\neq}/R} \tag{3.1}$$

where Λ is the membrane conductance, h is the plank constant, R is the gas constant, N is the Avagadro number and T is the obsolute temperature. $\Delta F^{\neq}$ is the free enrgy of activation for the diffusion of ions, and is related to the heat, $\Delta H^{\neq}$, and entropy of activation, $\Delta S^{\neq}$, by the Gibbs-Helmholtz equation:

$$\Delta F^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \tag{3.2}$$

$\Delta H^{\neq}$ is related to Arrhenius energy of activation E_a by

$$E_a = \Delta H^{\neq} + RT \tag{3.3}$$

A plot of $\log \Lambda Nh/RT$ versus $(1/T) \times 10^3$ (Figs.3.12 and 3.13) from experimental data gives a straight line, the slope and the intercept of which gives the value for $\Delta H^{\neq}/R$ and $\Delta S^{\neq}/R$ as demanded by eq. (3.1). This linearity justifies the applicability of eq. (3.1) to the system under investigation. The derived values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were then used to get the values of $\Delta F^{\neq}$ and E_a using eqs. (3.2) and (3.3). The values of various thermodynamic activation parameters E_a, $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $\Delta S^{\neq}$ derived in this way for the diffusion of various electrolytes in the membranes are given in Tables 3.13 and 3.14. The results indicate that the electrolyte permeation gives rise to negative values of $\Delta S^{\neq}$. According to
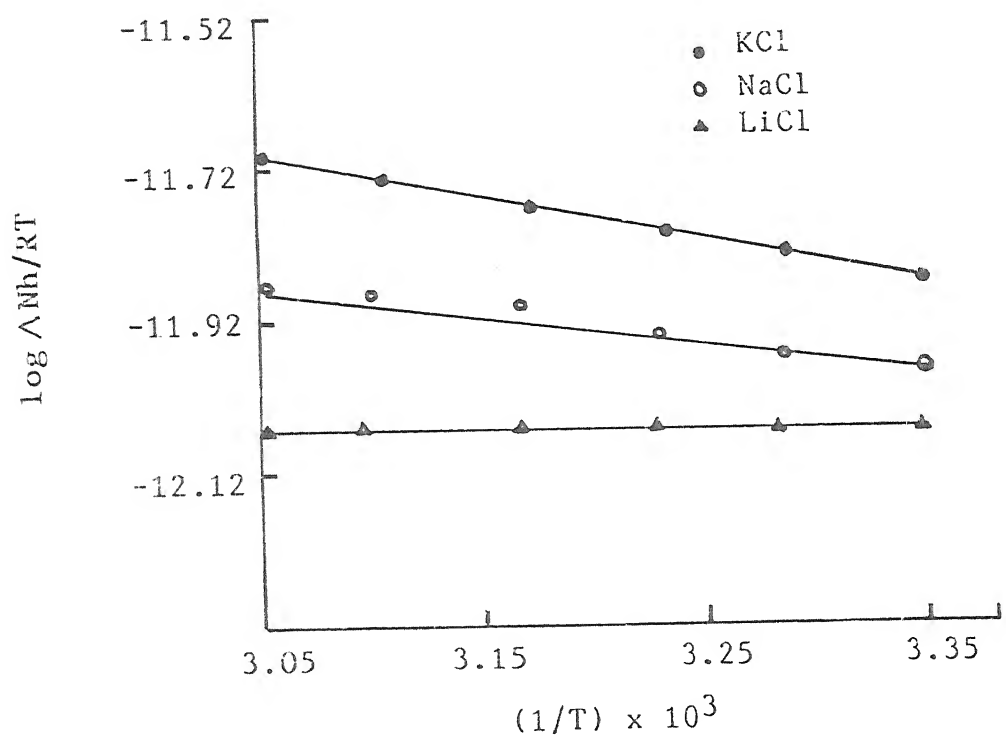
Fig. 3.12. Plots of log $\Lambda Nh/RT$ against $(1/T) \times 10^3$ for 0.1M solutions across mercuric sulphide membrane.
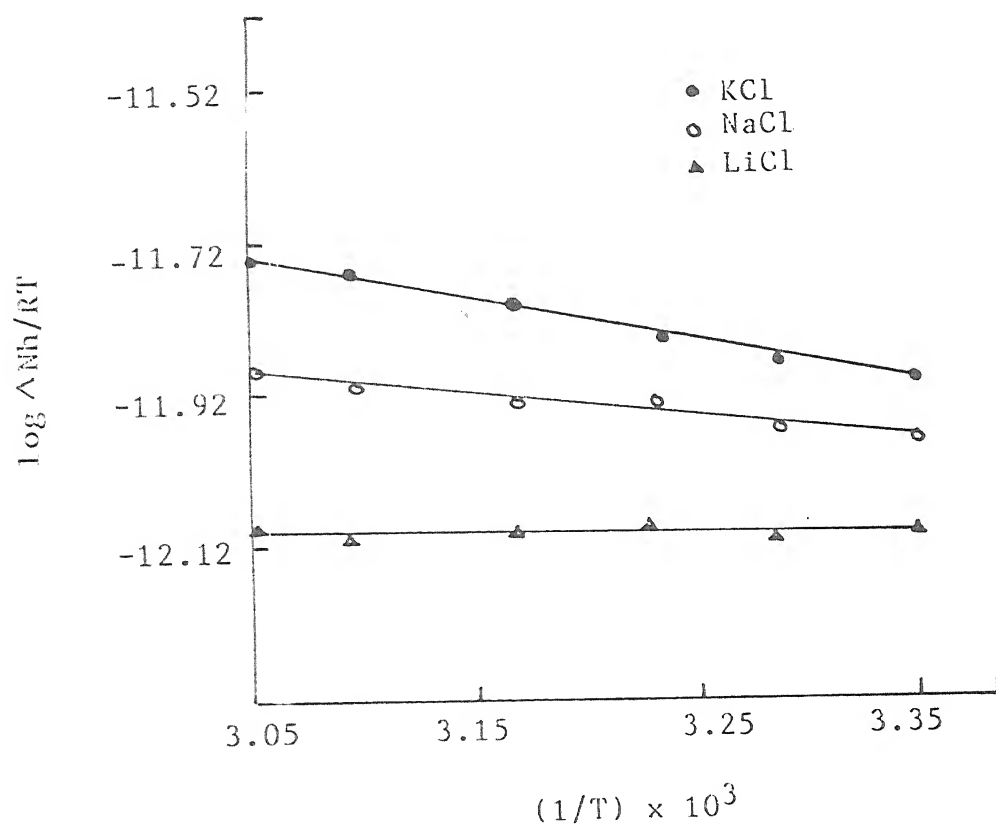
Fig.3.13. Plots of log $\Lambda Nh/RT$ against $(1/T) \times 10^3$ for 0.1 M solutions across nickel sulphide membrane.

Eyring and co-workers (28,58), the values of $\Delta S^{\neq}$ indicate that mechanism of flow; the large positive $\Delta S^{\neq}$ is interpreted as reflecting bonds breaking, white low values indicate that permeation has taken place without bonds breaking. Negative $\Delta S^{\neq}$ values are considered to indicate either formation of a covalent bond between the permeation species and the membrane material, or that the permeation through the membrane may not be the rate determining step (28).

On the other hand, Barrer (30,59,60) has developed the concept of "zone activation" and applied it to the permeation of gases through polymer membranes. According to this zone activation hypothesis, a high $\Delta S^{\neq}$ value, which has been correlated with high energy of activation for diffusion, means either the existance of a large zone of activation or the reversible loosening of more chain segments of the membranes. A low value for $\Delta S^{\neq}$, then, means either a small zone of activation or no loosening of the membrne structure upon permeations. In view of these differences in the interpretation of $\Delta S^{\neq}$, Schuler et al. (29), who found negative values of $\Delta S^{\neq}$ for sugar permeation through collodion membrane, have stated that "it would probabaly be correct to interpret the small negaative values of $\Delta S^{\neq}$ mechanically as interstitial permeation of the membrane (minimum chain loosening) with partial immobilization in the membrane (small zone of disorder)". On the other hand, Tien and Ting (7) who found negative $\Delta S^{\neq}$ values for the permeation of water through very thin (50 A$^{\circ}$ thickness)

bilayer membrane, stressed the possibility that the solution-membrane interface and not the membrane may be the rate determining step for permeation. Negative $\Delta S^{\neq}$ values may then be ascribed to the partial immobilization of ions and their interaction with the membranes fixed charge groups.

Contrary to this we have (61):

$$\Lambda = \Lambda_o \, e^{-E_a/RT} \tag{3.4}$$

$$\Lambda_o = 2.72 \, (KTd^2/h) \, e^{\Delta S^{\neq}/R} \tag{3.5}$$

Where K is the Boltzmann constant and d is the interionic jump distance, i.e. the distance between the equilibrium positions of diffusing species in the membranes. Equation (3.4) predicts that a plot of $\log \Lambda$ versus $1/T$ will give a straight line and E_a may be obtained. Substituting the value of parameters $\Delta S^{\neq}$ and E_a in eqs. (3.4) and (3.5) we obtain a value of interionic distance of about 1.5 A^o. This value of d is not unusual in these systems. Various investigetors (6,7,28,29,43,55,56,61) have used values of d ranging from 1 to 5 A^o.

The results of all these investigations are that membrane conductance can be determined at different temperatures with reasonable accuracy. The membranes are weakly charged and ionic species retain their hydration shell at least partially while diffusing through the membrane pores. Negative $\Delta S^{\neq}$ values suggest that the partial immobilization of ions takes place, due to most probably to interstitial permeation and ionic interaction with fixed charge groups on the membrane skeleton. The interionic jump distance for the system was 1.5 A^o.

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SUMMARY

Transport phenomena occuring across parchment suppor-
ted membranes have been thoroughly investigated by taking into
account the following aspects, namely (i) ionic transfer, (ii)
membrane potential, (iii) electrical conductivity, (iv) ionic
distribution equilibria and (v) spatial distribution of ions and
the potential within the membrane.

Many of the processes occuring in nature involve mem-
brane transport. Some of the functions perform by such membranes
appear to be unique,as well as efficient,and it could be possible
to make synthetic membrane having similar properties.Furthermore,
in this thesis an attention has been drawn to represent that
knowledge of synthetic membranes are extended to better under-
stand the changes which occur in biological ones. Also of inter-
est is the examination of the extent to which electroanalytical
methods may be applied to questions concerning the physical
chemistry of ion transport across membranes.

Synthetic and biological membranes are studied simul-
taneouly using the recently developed theories. Biological membr-
anes with the exception of cell membranes, are thinsheets of tis-
sue that cover various organs of body and plants of the hundreds
of biological membranes, one of the more familiar is the mucous
membrane.The mucous membrane functions as a barrier to keep toxi-
c components contracting one side of the membrane from tissue on
the other side but allows transport of species essential for the
tissue. Synthetic membranes are sub classified by composition,

function, structure and form. Composition refers to the material used to make the membrane i.e., organic or inorganic polymer. Functional classification of membranes includes gas separation, water desalination, dialysis etc. Form denotes whether the membrane is a film hollow fiber, tube, or coating.

The work done using mercuric and nickel sulphide parchment supported membranes and hen egg shell biological membrane has been devided into following three chapters. It is based on a more general approach to membrane transport, extended using the nonequilibrium thermodynamics.

Chapter I, deals with the characterization and evaluation of effective fixed charge density of mercuric, nickel sulphide parchment supported membranes and hen egg shell biological membrane from membrane potential measurements using various 1:1 electrolyte at different concentrations. The parchment supported membranes were prepared by the method of interaction adopted by syham et al. Hen egg shell membrane was separated from freshly laid down hen egg. The following methods for the evaluation of charge densities were utilized (i) Teorell-Meyer-Sievers method, (ii) the method developed by Kobatake and co-workers and (iii) the method of Nagasawa et al. based on the principle of nonequilibrium thermodynamics.

The values of membrane potential measured across mercuric and nickel sulphide membranes with the use of chlorides of potassium, Sodium and Lithium were all positive at lower concent-

rations,when the membranes were used to separate electrolytes (dilute solutions side taken as positive). However, at higher concentration of sodium and lithium chlorides respectively, membrane potential observed were negative. This means that membranes were a little bit anion selective at very higher electrolyte concentration. Moreover, the membrane potential values increase across the mercuric and nickel sulphide membranes with the dilution of electrolyte solutions. The membrane potential values observed across hen egg shell membrane using various 1:1 electrolyte solutions were negative at all concentration which confirms the anion selectivity of the membrane.

For the evaluation of effective fixed charge density, Teorell-Meyer and Sievers (TMS)derived a theoritical equation for membrane potential when a charged membrane separates different concentrations of an electrolyte by considering a diffusion potential within the membrane and two interfacial potentials at the membrane solution interfaces. The membrane potential equation, thus derived has been generally accepted and widely used for the evaluation of effective fixed charge density and mobitity ratio of the ions within the membranes by the plotting method. The method gave quite satisfactory results.

Kobatake, Noriaki and others derived an equation for membrane potential on the fixed charge concept by utilizing a number of basic assumptions. The two limiting forms of the equation were derived and used for the evaluation of fixed charge density

of the membranes.It was interesting to note that,the theoritical predictions were borne out quite satisfactorily by our experimental results with all the three membranes used in the investigations.

Another equation for membrane potential derived by Kobatake and Kamo, similar to the TMS equation was used for the evaluation of thermodynamically effective fixed charge density of the membranes. This method involves the use of apparent transference number of coions of the membrane.

On the other hand Tasaka, Nagasawa and co-workers derived another equation for membrane potential when a charged membrane separates two solutions of an electrolyte based on the principles of the irreversible thermodynamics. At sufficiently high electrolyte concentrations the equation reduces to a suitable form, which was used for the evaluation of effective fixed charge density of the membrane by the plotting method.

The values of effective fixed charge densities evaluated from different methods were identical.The values were low in confirmity with our results of diffusion rate studies.

Chapter II of the thesis describes the determination of the selectivity of the membranes for ions of electrolyte. Biionic potentials arising across parchment supported mercuric and nickel sulphide membrnes and hen egg shell membrane using various combinations of 1:1 electrolyte at different concentrations were measured. Intramembrane mobility ratio values were calculated

using the biionic potentials. The conductivity values of membranes with each single electrolyte were also determined experimentally in order to evaluate selectivity of the membranes using the predetermined values of the intramembrane mobility ratio. The equation for intramembrane mobility ratio and selectivity constant were derived by Wyllie, Sandblom and Eisenman from the mascroscopic laws of irreversible thermodynamis to calculate various membrane parameters. The selectivity sequence of the membrnes were found as $K^+ > Na^+ > Li^+$, which on the basis of the Eisenman-sherry model of membrane selectivity points towards the weak field strength of the charge groups attached to the membrane matrix. Theoritical membrane biionic potential values were also evaluated using the equation derived by Ilani and Wilson. This equation is in terms of fixed charge density along with other factors. The BIP values thus evaluated were similar to the practically observed values of biionic potential, values which conformed the validity of the membrane parameters. Moreover, biionic potential values of the membranes were also observed by varying the concentration of the electrolyte BX while keeping the concentration of electrolyte AX constant. Plotting these potentials against the activity ratio values of electrolytes, the order of membrane selectivity was found as $K^+ > Na^+ > Li^+$.

Capter III of the thesis covers transport mechanism of simple metal ions through the membranes. The linear phenomenological is a powerful tool to characterize membrane transport processes on the basis of the nonequilibrium thermodynamics. The

conductivity at different temperatures of parchment supported
mercuric and nickel sulphide membranes bathed in different con-
centrations of alkali metal chlorides have been reported and
using the absolute reaction rate theory transport mechanism of
simple metal ions through the membranes has been studied.

Experimentally observed specific conductance values of
the membranes increase linearly with concentrations up to a limi-
ting value at all temperatures. The flow of ions and water through
the membranes depends on diffusional path ways and fractional po-
re volumes. The order of conductance values for both the membranes
were found as $K^+ > Na^+ > Li^+$. On the other hand, values of specific
conductance of different electrolyte (chlorides) against free
energy of hydration of cations decrease with increasing hydration
energy, that is greater size due to increasing hydration. In
fact, it indicates that electrolyte is diffusing along pores with
dimensions adequate to allow the substance to penetrate the
membrane. The values of activation energy as required by Arrheni-
us equation have also been evaluated using the linear plots of
observed specific conductances against 1/T. These values decrease
with increasing concentration of the bathing electrolyte solution
and follows the order as:

$$E_{aK}^+ > E_{aNa}^+ > E_{aLi}^+$$

This order of activation energy represents the crystallographic
radii of the alkali metal cations. $\Delta F^{\ddagger}$ is the free energy of
activation for the diffusion of ions, is related to the heat $\Delta H^{\ddagger}$

and entropy of activation $\Delta S^{\neq}$ by the Gibbs-Helmholtz eqvation

$$\Delta F^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq}$$

$\Delta H^{\neq}$ is related to Arrhenius energy of activation E_a by

$$E_a = \Delta H^{\neq} + RT$$

In this way, the values of various thermodynamic parameters that is, activation energy E_a, $\Delta H^{\neq}$, $\Delta F^{\neq}$ and $\Delta S^{\neq}$ were derived similarly for the diffusion of various electrolytes in the membranes. The large positive value of $\Delta S^{\neq}$ is reflecting bonds breaking while low values indicate that permeation has taken place without bonds breaking. Negative $\Delta S^{\neq}$ values connect covalent bond formation, between the permeation species and the membrane material.

The results of all these investigations characterize, that the membranes are weakly charged and ionic species retain their hydration shell at least partially while diffusing through the membrane pores. The negative $\Delta S^{\neq}$ values suggest that the partial immobilization of ions takes place, due to most probably to interstitial permeation and ionic interaction with fixed charge groups on the membrane skeleton.

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Studies of inorganic precipitate membrane: Evaluation of membrane selectivity from bi-ionic potential and conductivity measurements

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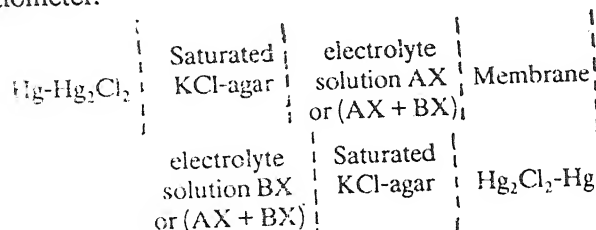B.B. (P.G.) Science College, Jhansi 284 001

Bi-ionic and multi-ionic potential across parchment supported mercuric sulphide membrane with various combinations of 1 : 1 electrolytes at different concentrations have been measured. Membrane conductivity in contact with a single electrolyte has been experimentally determined to evaluate the selectivity of the membrane with the predetermined values of the intra-membrane mobility ratio. The selectivity sequence of the membrane has been found as $K^+ > Na^+ > Li^+$ which on the basis of the Eisenman-Sherry model of membrane selectivity, points towards the weak field strength of the charge groups attached to the membrane matrix.

Effective fixed charge density of parchment supported membranes[1-7] and duck and hen egg shell membranes[8] has already been demonstrated using Eisenman-Sherry model[9,10] of membrane selectivity and the theories of membrane potential based on non-equilibrium thermodynamics. In this paper bi-ionic potential measurements across a parchment supported mercuric sulphide membrane have been carried out for the evaluation of membrane selectivity of ions. Membrane conductance in contact with various 1 : 1 electrolytes has also been experimentally determined to substantiate our findings.

Experimental

The membrane was prepared by the method of interaction described in part XI of this series[2]. The bi-ionic and multi-ionic potentials were measured by constructing an electro-chemical cell of the following type with a pye precision vernier potentiometer:

Hg-Hg₂Cl₂	Saturated KCl-agar	electrolyte solution AX or (AX + BX)	Membrane
	electrolyte solution BX or (AX + BX)	Saturated KCl-agar	Hg₂Cl₂-Hg

Aqueous solutions of sodium, potassium and lithium chlorides (BDH, AR grade) were used on the two sides of the membrane and were vigorously stirred with a pair of electrically operated magnetic stirrers to remove completely or at least to minimize the effect of the film controlled diffusion[11].

Electrical conductivity of the membrane was determined by setting up a cell of the type shown in Fig. 1 with a conductivity bridge (Cambridge Instrument, England). All measurements were carried out at $25 \pm 0.1°C$. The error in measurement of membrane potential was within $\pm 1\%$ whereas electrical conductivity could be measured to better than 99.5% accuracy.

Results and discussion

When an ion exchange membrane of different concentrations is interposed between two solutions of an electrolyte the mobile species penetrate the membrane and various transport phenomena are introduced into the system[12]. If the membrane is used to separate the solutions of the type AX and BX (or AX and AY) electrolytes the steady potential developed is called bi-ionic[13] which is a measure of the selectivity of the membrane for ions of the same sign. Bi-ionic potential has been considered by Helfferich[14], according to the concepts of the TMS theory[15,16] as being the algebraic sum of two interfacial potentials and an internal diffusion potential. For a general case the total bi-ionic potential E for counterions of equal valencies by Wyllie and Kanaan[17] is given by Eq. (1)

$$E = \frac{RT}{F} \ln \frac{a_i \overline{U}_i}{a_j \overline{U}_j} \qquad \cdots (1)$$

where a_i/a_j and $\overline{U}_i/\overline{U}_j$ are the activity ratio of the solutions and mobility ratio of the ions in the mem-
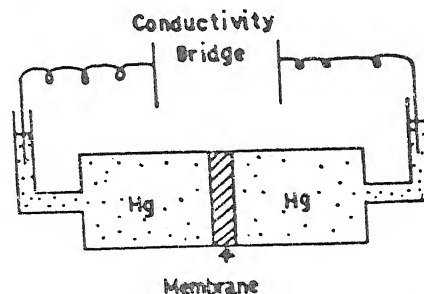

Fig. 1—Experimental cell

brane phase respectively. Wyllie[18] expressed the intramembrane mobility ratio as:

$$\frac{\overline{U}_i}{\overline{U}_j} = \frac{\bar{t}_i}{\bar{t}_j} = \frac{\bar{m}_i \overline{\lambda}_i}{\bar{m}_j \overline{\lambda}_j} \qquad \ldots (2)$$

where $\bar{t}_i/\bar{t}_j$ is the intramembrane transference ratio and $\bar{m}_i$ and $\bar{m}_j$ are the steady state equilibrium concentration of i and j in the respective zone; $\overline{\lambda}_i$ is the conductivity of the membrane when it is wholly in i form and $\overline{\lambda}_j$ is the conductivity of the membrane when it is wholly in j form. Furthermore, it was shown that $\bar{m}_i/\bar{m}_j \approx K_{ji}$ is the selectivity. This, on substitution into Eq. (2) gives

$$\frac{\overline{U}_i}{\overline{U}_j} = K_{ji}\left(\frac{\overline{\lambda}_i}{\overline{\lambda}_j}\right) \qquad \ldots (3)$$

Thus, the ratios of mobilities were related to the chemical and electrical properties of the membrane.

Bi-ionic potential measurements were also carried out by interposing the membrane between two different electrolyte solutions at the same concentration. The values of bi-ionic potential across parchment supported mercuric sulphide membrane with various 1 : 1 electrolyte combinations at different concentrations are shown in Fig. 2. The values of intramobility ratio $\overline{U}_i/\overline{U}_j$ calculated using Eq. (1) are given in Table 1. An interestng point with regard to the value of $\overline{U}_i/\overline{U}_j$ is that the mobility ratio undergoes considerable change with the concentration of the each electrolyte pair.

To gain knowledge of selectivity K_{ji} from the predetermined values of $\overline{U}_i/\overline{U}_j$ the ratio of electrical conductivities $\overline{\lambda}_i/\overline{\lambda}_j$, demanded by Eq. (3), must be known. Membrane conductance measurements were carried out when it was wholly in form i or from j. The values of membrane conductance

(Fig. 3) were relatively more dependent on the concentration of the electrolytes which implies that the membrane has a relatively high Donnan uptake of anion and a low selectivity constant values. The values of selectivity K_{ji} evaluated using the values of electrical conductivity and the intramembrane mobility ratio from Table 1 are given in Table 2. The intramembrane mobility ratio values also refer to the selectivity sequence of the membrane for the cations $K^+ > Na^+ > Li^+$. This order of selectivity on the basis of the Eisemnan-Sherry model of membrane selectivity[9,10] points towards the weak field strength of the charge groups attached to the membrane matrix. Further, it is well known that the bi-ionic potential is a measure of selectivity[19] of a membrane for ions of the same sign. Equation (4) has been found to predict the values of bi-ionic potential reasonably well
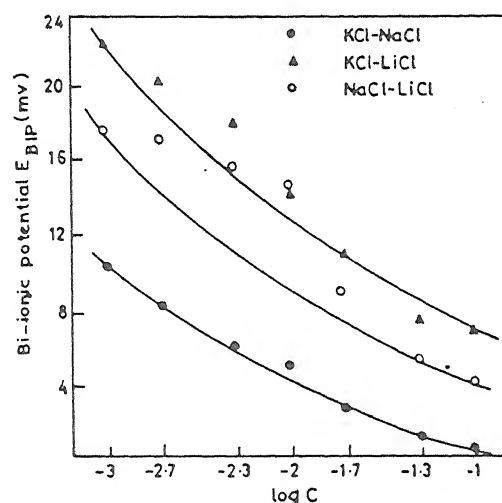

Fig. 2—Plots of bi-ionic potential E_{BIP} (mV) versus log C across mercuric sulphide membrane with 1 : 1 electrolytes
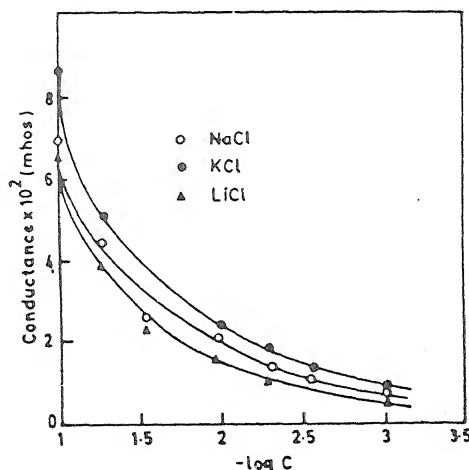

Fig. 3—Plots of conductance × 10² (MHOS) versus log C for mercuric sulphide membrane with 1 : 1 electrolytes

Table 1—Values of the intramembrane mobility ratios of various 1 : 1 electrolyte ions pairs

Membrane	Mercuric sulphide		
Electrolyte ion pair	$\overline{U}_{K^+}/\overline{U}_{Na^+}$	$\overline{U}_{K^+}/\overline{U}_{Li^+}$	$\overline{U}_{Na^+}/\overline{U}_{Li^+}$
Concentration (M)			
0.1/0.1	1.01	1.32	1.17
0.05/0.05	1.04	1.34	1.22
0.02/0.02	1.10	1.53	1.42
0.01/0.01	1.21	1.74	1.75
0.005/0.005	1.27	1.99	1.83
0.002/0.002	1.38	2.21	1.94
0.001/0.001	1.52	2.39	1.97

Table 2—Values of the selectivity K_{ji} $(1/K_{ij})$ evaluated from the intramembrane mobility ratio and the ratio of electrical conductivities at various electrolyte concentrations

Membrane	Mercuric sulphide						
Concentrations (M)	0.1/0.1	0.005/0.05	0.02/0.02	0.01/0.01	0.005/0.005	0.002/0.002	0.001/0.001
Selectivity							
K_{NaK}	0.83	0.89	0.98	1.10	0.90	1.25	1.38
K_{LiK}	1.00	1.05	1.30	1.58	1.26	1.90	1.65
K_{LiNa}	1.09	1.10	1.30	1.40	1.60	1.80	1.47

provided $\overline{\gamma}_B/\overline{\gamma}_A$ remains constant.

$$E_{BIP} = \frac{RT}{F} \ln \frac{\overline{U}_A a'_A \overline{\gamma}_B}{\overline{U}_B a''_B \overline{\gamma}_A} \qquad \ldots (4)$$

Equation (4) can be written as

$$E_{BIP} = \frac{RT}{F} \ln \frac{\overline{U}_A a'_A}{\overline{U}_B a''_B} \quad (\text{if } \overline{\gamma}_A = \overline{\gamma}_B) \qquad \ldots (5)$$

and

$$E_{BIP} = \frac{RT}{F} \ln \frac{\overline{t}_A}{\overline{t}_B} \qquad \ldots (6)$$

where $\dfrac{\overline{t}_A}{\overline{t}_B} = \dfrac{\overline{u}_A \overline{a}_A \overline{\gamma}_B}{\overline{u}_B \overline{a}_B \overline{\gamma}_A}$

provided that the Donnan relation $\overline{a}_A/\overline{a}_B = a'_A/a''_B$ is established.

The bi-ionic potentials generated across mercuric sulphide membrane were also measured by keeping the concentration of AX constnat and by varying the concentration of BX, and again by keeping [BX] constant and varying [AX]. These measurements were extended to three solutions, i.e. KCl-NaCl, KCl-LiCl and NaCl-LiCl. The bi-ionic potential values thus masured were plotted in Fig. (4) as a function of log a_{AX}/a_{BX}. Good linear plots as demanded by Eq. (5) were obtained. The point of intersection of the two linear plots at the same activity, i.e., $a_{AX}/a_{BX} = 1$, gives the value of the transport ratio using Eq. (6). The transport ratio thus obtained for different 1 : 1 electrolyte pairs are

$$\overline{t}_{K^+}/\overline{t}_{Na^+} = 1.12, \overline{t}_{K^+}/\overline{t}_{Li^+} = 1.08, \overline{t}_{Na^+}/\overline{t}_{Li^+} = 1.06.$$

These results also point towards the order of selectivity of cations transporting through the membrane as: $K^+ > Na^+ > Li^+$.

Acknowledgement
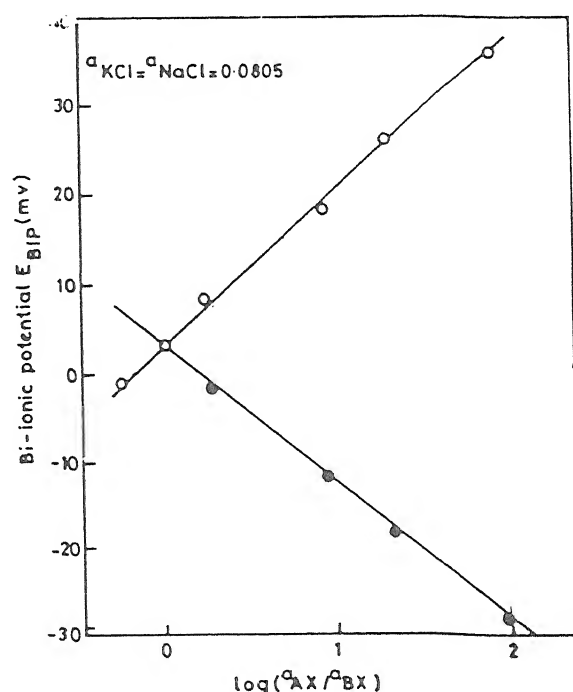
Fig. 4—Plots of log (a_{AX}/a_{BX}) versus bi-ionic potential E_{BIP} (mV) for KCl-NaCl set

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Abstract of the paper orally presented in the annual conference
of Indian Council of Chemists held at Gulbarga (Karnatka) on
December 1990.

TITLE :-

STUDIES OF INORGANIC PRECIPITATE MEMBRANE : TEST OF
BIIONIC POTENTIAL THEORY AND THE EVALUATION MEMBRANE SELECTIVITY
FROM BIIONIC AND CONDUCTIVITY MEASUREMENTS.

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ABSTRACT

It has been known for a long time that porous membranes
impregnated with inorganic precipitates, separating solutions of
an electrolyte at two different concentrations, record potential
differences which are different from the normal liquid junction
potentials. Biionic and multiionic potentials across parchment
supported mercuric sulphide membrane with various combinations of
1:1 electrolytes at different concentrations were measured.
Membrane conductivity in contact with a single electrolyte was
experimentally determined to evaluate the selectivity of the
membrane with the predetermined values of the intramembrane
mobility ratio. The selectivity sequence of the membrane was
$K^+ > Na^+ > Li^+$ which on the basis of the Eisenman-Sherry model of
membrane selectivity, points towards the weak field strength of
the charge groups attached to the membrane matrix. Biionic

potential theory was tested using the predetermined values of membrane charge density and aforesaid selectivity sequence was also confirmed.

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STUDIES WITH INORGANIC PRECIPITATE MEMBRANE : EVALUATION OF EFFECTIVE FIXED CHARGE DENSITY AND TEST OF MEMBRANE POTENTIAL AND BIIONIC POTENTIAL THEORIES BASED ON NON-EQUILIBRIUM THERMODYNAMICS.

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ABSTRACT

It has been known for a long time that porous membranes impregnated wit inorganic precipitates, separating solutions of an electrolyte at two different concentrations, record potential differences which are different from the normal liquid junction potentials, Transport phenomena in membranes have attracted the attention of chemists, biochemists, biophysicists, pharmacologists, physiologist and Industrial Engineers etc. Memb·ane potential measurements across parchment supported mercuric sulphide membrane in contact with various 1:1 electrolytes have been carried out in order to evaluate the

thermodynamically effective fixed charge density by most recent method of Nagasewa et al. The theoritycal equations based on non equilibrium thermodynamics for membrane potential and bi-ionic potential derived by ToyoShima and Nozaki have also been applied and tested with mercuric sulphide membrane. It was found that the theoritically calculated bi-ionic potentials agree well with the experimentally observed values.

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